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Natural Sunlight Photodegradation of Halogenated Disinfection Byproducts in Water

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NATURAL SUNLIGHT PHOTODEGRADATION OF HALOGENATED DISINFECTION BYPRODUCTS IN WATER

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This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy in Civil Engineering degree and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this dissertation does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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بسم الله الرحمن الرحيم

(وَقُلِ اعْمَلُوا فَسَيَرَى اللَّهُ عَمَلَكُمْ وَرَسُولُهُ وَالْمُؤْمِنُونَ)
صدق الله العظيم

إلهي لا يطيب الليل إلا بشكرك و لا يطيب النهار إلى بطاعتك .. و لا تطيب اللحظات إلا بذكرك .. ولا تطيب الآخرة إلا بعفوك .. ولا تطيب الجنة إلا برؤيتك
فاياربي لك الحمد والشكر

اهداء

إلى التي أعطتني من دمها وروحها وعمرها حبا وتصميما ودفعا لغدٍ أجمل
إلى ينبوع الصبروالتفاؤل
إلى الغالية التي لا نرى الأمل إلا من عينيها أمي الحبيبة

إلى من جرع الكأس فارغاً ليسقيني قطرة حب
إلى من كلّت أنامله ليقدم لي لحظة سعادة
إلى من حصد الأشواك عن دربي ليمهد لي طريق العلم
إلى القلب الكبيروالدي العزيز

إلى من آثروني على نفسهم
إلى من علموني علم الحياة
إلى من أظهروا لي ما هو أجمل من الحياة إخوتي

To my family

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ABSTRACT

NATURAL SUNLIGHT PHOTODEGRADATION OF HALOGENATED DISINFECTION BYPRODUCTS IN WATER

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Disinfection byproducts (DBPs) presence in wastewater effluents and receiving waters may impact the quality of drinking water during water reuse practices. Natural solar photolysis is one of the biogeochemical processes that may lead to decreased DBPs concentrations in water. The purpose of this dissertation is to determine the fate of chlorinated, brominated and iodinated DBPs in surface water by natural sunlight photolysis and investigate the use of solar-based advanced oxidation processes (AOPs) for removal of DBPs in water.

Total organic halogen (TOX) was used to measure total chlorinated- (TOCl), brominated- (TOBr) and iodinated-DBPs (TOI) in water. The first objective was to determine the optimum protocol for TOX sample preservation conditions to ensure accurate TOX analysis throughout the following experiments. To achieve the highest TOX recovery, samples must be stored at pH 2 using nitric acid, 4 °C incubator and be analyzed within 14 days of storage. Overdosing of quenching agents such as sodium sulfite, sodium thiosulfate and ascorbic acid must be avoided to maintain stable TOX concentrations during storage.

The second objective was to determine the fate of TOCl, TOBr, TOI and individual DBPs by natural sunlight in surface water. Iodinated DBPs were the most photodegradable specific halogenated DBPs, whereas chlorinated DBPs were the most

resistant to sunlight photodegradation. The TOX degradation rates were generally in the order of TOI > TOBr ≅ TOCl(NH_2Cl) > TOCl(Cl_2) and the half-lives ranged between 2.6 and 10.7 h during solar photolysis. Typical concentrations of natural surface and wastewater containments including nitrate, nitrite and sulfite had little impact on enhancing DBPs photodegradation rates. However, natural organic matter and turbidity decreased photodegradation of DBPs by light screening.

The third objective was to evaluate the use of solar-based AOPs for DBP removal in water. Both solar-TiO_2 photocatalytic and solar photo-fenton processes increased DBPs photodegradation rates significantly in comparison to solar photolysis alone. TOX half-lives were reduced from hours to minutes by the two solar-based AOPs, and the rate of degradation were generally in the order of TOI > TOCl(NH_2Cl) > TOBr > TOCl(Cl_2). Oxidation by hydroxyl radicals is expected to be the main mechanism accountable for improved DBP degradation. Furthermore, several natural water constituents including chloride, sulfate, natural organic matter and bicarbonate decreased DBPs degradation efficiency by solar-based AOPs.

CHAPTER ONE
INTRODUCTION

1.1 Background

Drinking water supplies around the world are under increasing pressure due to the impact of population growth, climate change, pollution and land geographical changes that affected water quality and quantity. These impacts lead to anticipated drinking water shortages in communities around the world. To address this issue, many communities have considered water conservation through reclamation, reuse and recycling of treated wastewater to augment drinking water supplies (Rodriguez et al. 2009). However, unintentional indirect reuse of wastewater has taken place for many decades. Upstream wastewater treatment plants (WWTPs) discharge treated wastewater effluent to downstream surface water (river, lake, etc.) that is directly used by drinking water treatment plants (DWTPs) to provide drinking water to communities. Currently, almost one quarter of treated wastewater effluents are discharged to surface water with ten or less dilution factor (Brooks et al. 2006). Therefore, the contaminants present in the treated wastewater effluent may affect the quality of the drinking water and cause serious health risks to public and marine life (Dominguez-Chicas and Scrimshaw 2010, Snyder et al. 2003). Furthermore, indirect water reuse is expected to increase in the near future and thus the contaminants impact, since the number of operated WWTPs in US are expected to increase to reach 15,122 in 2032 to cover roughly 80% of population, in contrast with 14,581 in 2012, according to the 2012 Clean Watershed Needs Survey of the United States Environmental Protection Agency (USEPA) (USEPA 2012). Therefore, it's

important to remove wastewater effluent contaminants prior to discharge into surface water to protect the public health and the aquatic ecosystem.

Of all contaminants present in wastewater effluent, halogenated disinfection byproducts (DBPs) are a group of carcinogenic and genotoxic organic compounds that form during the disinfection practice at WWTPs (Krasner et al. 2009). DBPs have been under environmental examination by researchers, water and wastewater practitioners for the last several decades in an effort to understand their chemical characteristics, toxicity, stability and formation and degradation potential in water (Xie 2016). As a result of extensive research, the EPA in 2006 has regulated some groups of DBPs in drinking water to reduce the health risks associated with exposure to DBPs. Therefore, it is essential to remove wastewater derived DBPs to limit their presence in drinking water during water reuse practices.

In aquatic systems, DBPs concentrations are attenuated under several natural degradation mechanisms including biodegradation, hydrolysis, adsorption, volatilization and solar photolysis (Chen et al. 2008). However, utilization of natural sunlight for treatment purposes has gained substantial importance in the last decades due to several advantages over competing treatment processes including increased cost-efficiency, environmental safety, effectiveness and the ability to be combined with catalysts to achieve higher removal rates of targeted toxic compounds. Therefore, the purpose behind this dissertation is to investigate the fate of halogenated DBPs under natural sunlight irradiation in drinking water supplies and to design an advanced treatment system that utilizes natural sunlight along with catalysts to achieve complete removal of DBPs in wastewater effluent prior to discharge.

1.2 Formation of DBPs

The addition of chlorine during the disinfection practice at WWTPs has produced safe treated wastewater effluent to discharge into surface water, by deactivating microorganisms that cause water-borne diseases. However, the use of chlorine or other chemical disinfectants including chloramine, chlorine dioxide, ozone and others has additionally caused unintended health hazards for the public such as birth defects, bladder and colorectal cancers and others that are linked with the presence of halogenated DBPs (Richardson and Ternes 2017, Villanueva et al. 2004).

In 1974, it has been discovered that chlorine (the most widely used disinfectant since 1900s) can react with naturally existing organic matter (NOM) in water leading to the formation of DBPs. NOM is a mixture of fulvic and humic acids that leach from decayed plants, leaves, algae and microorganisms, and serve as a primary precursor for DBP formation in water. Chlorine gas or solution rapidly dissolves in water to form reactive hypochlorous acid (HOCl). HOCl is a powerful oxidant due to its chemical structure characterized by Cl-O bond polarization, and thus can react with the majority of organic compounds through oxidation reactions, addition reactions to unsaturated bonds, and electrophilic substitution reactions at nucleophilic sites. At a pH values lower than 7.5, HOCl is the dominant species in contrast with hypochlorite ions which are less oxidative ion compared to HOCl (Deborde and Von Gunten 2008).

$$Cl_2 + H_2O \leftrightarrow HOCl + Cl^- + H^+$$

$$HOCl \leftrightarrow ClO^- + H^+$$

In addition to NOM oxidation to produce chlorinated DBPs, HOCl can also oxidize inorganic ions including bromide and iodide, that are present in surface water. Bromide and iodide presence are directly linked to the wastewater discharges from coal powered electrical plants, oil-field brines and hospitals. In addition, salt water intrusion into water supplies near coastal areas can increase their levels. Reaction of HOCl with bromide and iodide leads to the production of hypobromous acid (HOBr) and hypoiodous acid (HOI) (Hua et al. 2006) that subsequently react with NOM to produce brominated and iodinated DBPs, respectively (Barceló 2012, Duirk et al. 2011, Krasner et al. 2009, Parker et al. 2014, VanBriesen 2014). New epidemiologic studies reported that brominated and iodinated DBPs are related to higher cancer, developmental and reproductive effects compared to chlorinated DBPs (Richardson et al. 2007, Yang et al. 2014). Therefore, the combination of chlorinated, brominated and iodinated DBPs after chlorination of wastewater effluent can harm the biological life in surface waters and affect the quality of drinking water (Watson et al. 2012, Yang et al. 2015).

THMs such as chloroform were the first group of organic DBPs to be discovered in drinking water, and soon after discovery; it was initially regulated in US by 1979 at 100 µg/L in finished drinking water since it caused cancer in laboratory. Afterwards, another group of organic DBPs, including HAAs, were also regulated and their regulations were adopted by other countries around the world. THMs and HAAs are often referred to as THM4 and HAA5, respectively, referring to the four regulated THMs including chloroform, bromoform, bromodichloromethane and dibromochloromethane and five regulated HAAs including mono-, di- and trichloroacetic acid and mono-,

dibromoacetic acid. Table 1.1 demonstrates the current regulations for THMs and HAAs in US, Europe and the World Health Organization (WHO).

Chlorine and chloramine are the main disinfectants accountable for the highest formation of THMs and HAAs in drinking water, however, chlorine is also responsible for the formation of other groups of unregulated halogenated DBPs including halonitromethanes (HNMs), haloacetonitriles (HANs), trihaloacetaldeydes (THAs), haloketones (HKs), halonitrophenols, haloacetamides, nitrosamines and others (Hua and Reckhow 2007, Krasner et al. 2009, Yang and Zhang 2013). In total, more than 800 DBPs have been identified in the literature when chlorine, chloramine, chlorine dioxide or ozone used in drinking water disinfection practice (Čulin and Mustać 2015, Hebert et al. 2010, Richardson 2011). However, less than 100 have been examined and studied for toxicity (Barceló 2012). Epidemiologic studies concluded that many of the unregulated DBPs are much more toxic than the regulated ones (Li et al. 2016, Li and Mitch 2018, Richardson and Ternes 2017, Yang and Zhang 2013). Therefore, there was a need for a tool that can measure total halogenated DBPs concentration in drinking water and indicate for total DBPs toxicity. This led to the development of the total organic halogen (TOX) analyzer.

TOX measures total concentration of halogenated materials in water, and when paired with ion chromatography, TOX can be differentiated into halogen-specific TOX compounds including total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI) (Hua and Reckhow 2006, Kristiana et al. 2015). In chlorinated drinking water, studies reported that individual known DBPs including THMs, HAAs and others account for roughly 50% of the TOX measured, where the other 50% are unknown DBPs. THMs and

HAAs accounted for the most known fraction of chlorinated TOX with 23% and 22%, respectively (Figure 1.1). On the other hand, known DBPs accounted for only 20% of TOX formed by chloramine, where the other 80% are unknown DBPs. HAAs including dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) are the major fraction of known chloraminated TOX with approximately 14% total (Figure 1.2) (Hua and Reckhow 2007, 2008a).

Increasing attention has been given to identify the unknown DBPs or unknown total organic halogen (UTOX), since most of the unregulated DBPs demonstrated higher toxicity than regulated ones. Research demonstrated that UTOX consist mostly of higher molecular weight aromatic DBPs (MW > 1000 Da) such as halobenzoquinones (HBQs), chlorophenylacetonitriles (CPANs) and others that have been recently discovered in chlorinated and chloraminated water, which also induced higher genotoxicity and cytotoxicity than regulated THMs and HAAs (Li et al. 2015, Xiao et al. 2012, Zhai et al. 2014, Zhang et al. 2018, Zhang and Minear 2002). However, more research and new analytical techniques are still needed to characterize UTOX in drinking water. Therefore, TOX is an excellent method for measurement of known and unknown DBPs in drinking water regardless of their identification, and also has been recognized as DBP toxicity indicators in water. Several studies showed that TOX levels in water samples are positively correlated with toxic potency in disinfected water, where higher TOX recoveries in water samples induced higher genotoxicity and cytotoxicity (Han and Zhang 2018, Itoh et al. 2011, Li and Mitch 2018, Stalter et al. 2016, Yang et al. 2015).

In addition to the measurement of the unknown DBPs, TOX capability to measure TOBr and TOI in water samples, increase the importance of TOX analysis in water and

wastewater treatment. Brominated and iodinated DBPs are now under examination due to their higher toxicity than their chlorinated analogues, and their presence in water is not only reported in wastewater and surface water, but also in drinking water supplied from sea and brackish waters (Ding et al. 2013, Gong et al. 2018, Yang et al. 2015). Therefore, removal of chlorinated, brominated and iodinated DBPs from wastewater effluent and surface water is an essential step to protect drinking water supplies, public health and aquatic ecosystem from the health hazards associated with exposure of DBPs.

1.3 Degradation of DBPs in Natural Surface Water

The stability of DBPs in aquatic systems can be altered under the impact of several natural degradation mechanisms including volatilization, hydrolysis, adsorption, biodegradation and solar photolysis. Volatilization has been reported to be effective in reducing THMs in stream-type watershed, where adsorption mechanism was insignificant to degrade DBPs. Hydrolysis effect on DBPs concentration are based on the halogen associated with the DBP ($I^- > Br^- > Cl^-$), and DBP side group, where degradation increased as follow for: HKs > HANs > HAs > HAAs > THMs. Biodegradation was effective in decreasing HAAs concentrations in biomass-rich water. Finally, NAs were rapidly photolyzed under natural sunlight exposure.

Several studies reported that sunlight irradiation can also induce photodegradation for other groups of DBPs, where degradation potential depend on many factors including light intensity, water depth, chemical structure of the specific DBPs and others. However, due to the many advantages of using natural sunlight including wide availability, cost-effective, environmentally friendly and others, its currently under wide investigation and consideration for water and wastewater treatment applications for removal of toxic

organic compounds including DBPs. Furthermore, natural sunlight can be utilized to induce chemical degradation in the presence of catalyst (TiO_2, SO_3^{2-}, Fe^{3+} and others), where it can absorb sunlight energy to produce highly oxidative or reductive radicals including hydroxyl-, hydrated electron radicals and others that might lead to significant increase in degradation. This section covers state of literature on the degradation of DBPs by photolysis processes.

1.4 Photolysis of DBPs

1.4.1 Trihalomethanes and Haloacetic acids

In literature, the photolytic studies conducted on halogenated methane used either artificial light such as UV light, simulated sunlight or natural sunlight. A study by Nicole 1991 on THMs photodegradation using UV at 253.7 nm, 20 °C and pH 7.5 resulted in rapid losses for bromoform ($CHBr_3$), bromodichloromethane ($CHBrCl_2$) and dibromochloromethane ($CHBr_2Cl$), where chloroform ($CHCl_3$) showed high stability (> 5% degradation). Similar results were also reported by (Jo et al. 2011), where bromoform was the most sensitive to UV 253.7 nm followed by $CHBr_2Cl$ and $CHBrCl_2$ and no apparent degradation for chloroform. Furthermore, the use of higher UV wavelength (> 350 nm) also led to the same conclusion where THMs degradation rates increased as follow for bromoform > $CHBr_2Cl$ > $CHBrCl_2$ > chloroform, where the rate constants ranged between 0.02 and 0.394 min^{-1}(Hansen et al. 2013). Another study examined the photodegradation of 6 iodinated- and 3 brominated-THMs under UV 254 nm irradiation. The results showed that photodegradation rate constants for non-chlorinated THMs including $CHBr_2I$, $CHBrI_2$ and CHI_3 were higher than chlorinated/iodinated THMs ($CHCl_2I$, CHClBrI, and $CHClI_2$) and the brominated/chlorinated THMs ($CHBr_3$, $CHCl_3$,

$CHCl_2Br$, $CHCl_2Br$). Iodinated THMs reported first-order rate constants in the range of 0.1-0.6 min^{-1} (Xiao et al. 2014).

Few studies investigated halogenated methane degradation under sunlight irradiation. A study by Chen et al. 2010 examined photodegradation of several group of DBPs including THMs under natural and simulated sunlight. Bromoform, $CHBr_2Cl$ and $CHBrCl_2$ were found degraded at rates of 0.21, 0.156 and 0.098 h^{-1}, respectively, under natural sunlight at 30 °C, whereas chloroform was hardly degraded. Furthermore, losses of iodinated dihalomethanes including CH_2I_2, CH_2IBr and CH_2ICl under natural solar photolysis were examined and resulted in degradation rate constants of 4.32, 0.145 and 0.078 h^{-1}, respectively (Jones and Carpenter 2005). In general, the photolysis potential of halogenated methane under artificial light or sunlight is positively correlated to the size of substituted halogen (I > Br > Cl) and on the number of halogen atom inside a halogenated compound (tri > di > mono) (Chen et al. 2010, Chuang et al. 2016, Martino et al. 2005, Xiao et al. 2014). The mechanism of halogenated methane photodegradation is believed to be a substitution of halogen atom on the parent compound with hydroxide group, leading to the formation of methanol and halide ion (Castro and Belser 1981, Chen et al. 2010, Jones and Carpenter 2005).

On the other hand, HAAs photodegradation were also examined under the impact of sunlight irradiation and reported generally to be insignificant. Chen et al. 2010 reported < 20% degradation under natural sunlight for brominated and chlorinated DBPs, however, chlorinated species were observed to be more resistant than brominated. This also agreed with another study by (Lifongo et al. 2004) where HAAs stability were investigated under simulated sunlight, which resulted in rate constants of 3×10^{-3}, 6.91 x

10^{-4}, 2.3 x 10^{-4} and 1.84 x 10^{-4} h^{-1} for tribromoacetic acid (TBAA). dibromoacetic acid (DBAA), trichloroacetic acid (TCAA) and bromochloroacetic acid (BCAA), respectively. However, monohalogenated HAAs including monochloroacetic acid (MCAA) and monobromoacetic acid (MBAA) showed no photodegradation. However, HAAs showed higher degradation rates under UV irradiation. A recent study by Wang et al. 2017 showed degradation rate constants of 0.0057-0.245 min^{-1} for chlorinated, brominated and iodinated HAAs, where degradation rates followed the orders of I-> Br- > Cl-HAAs with the same number of halogens, and tri > di > mono HAAs with identical types of halogen (Chen et al. 2015, Chuang et al. 2016, Li et al. 2012. Similar results were also observed by Jo et al. 2011 and Wang et al. 2009) where Cl-HAAs were more resistant to photolysis rates than Br- and I-HAAs, due to the difference in bonds strength where C-Cl is stronger than C-Br that stronger than C-I (Chen et al. 2015, Chuang et al. 2016). Regarding the end products, it is expected that Br- and I-HAAs undergo dehalogenation of C-X bonds, followed by nucleophilic addition and decarboxylation of C-C bonds leading to the formation of halogenated free organic compounds (Bu et al. 2018, Jo et al. 2011, Wang et al. 2009, Wang et al. 2017). Where Cl-HAAs may undergo some losses by two degradation mechanisms including dehalogenation of C-Cl bonds and decarboxylation of C-C bonds simultaneously, since it had been reported that C-Cl and C-C bonds contain similar energy bonds, thus, leading to higher loss of organic content (TOC) as observed during DCAA photodegradation (Wang et al. 2017, Zalazar et al. 2007).

1.4.2 Haloketones and Haloacetaldehydes

Haloketones (HKs) and haloacetaldehydes (HAs) have been examined under photolysis processes. Photodegradation of HKs such as 1,1-dichloropropanone (DCP) and 1,1,1-trichloropropanone (TCP) have been reported very few in the literature. In a study by Chen et al. 2010, TCP and DCP showed photodegradation of < 15% under sunlight irradiation at neutral pH and 30 °C. However, the results were inconclusive since TCP and DCP in dark degraded significantly due to hydrolysis. Another study by Lekkas and Nikolaou 2004 showed adverse effects of TCP under sunlight, where TCP concentrations increased instead of degradation. Furthermore, the use of medium pressure UV light did not affect TCP and DCP stability in water where their rate constants (0.019, 0.022 min^{-1}) were similar to chloroform (0.02 min^{-1}) (Hansen et al. 2013).

Haloacetaldehydes are group of DBPs that reported to present in treated waters including chloral hydrate (CH, trichloroacetaldehyde), tribromoacetaldehyde (TBA), dibromoacetaldehyde (DBA) and bromodichloroacetaldehyde (BDCA) (Koudjonou and LeBel 2006). Under solar photolysis, TBA, DBA and BDCA exhibited rate constants of 0.07, 0.017 and 0.011 h^{-1}, respectively, indicating increase in photodegradation rates with increase bromine incorporation (Chen et al. 2010). On the contrary, Lekkas and Nikolaou 2004 reported increase in CH concentrations under similar solar photolysis conditions. However, using low pressure UV at 254 nm irradiation, CH photodegradation reported rate constants of 0.144 to 3.06 h^{-1} when pH increased from 7 to 10.5 at lamp power of 6 W. Moreover, CH photodegradation rates were doubled when 12 W of lamp power used (Gan et al. 2019). This also agreed with another study where CH photodegradation rate constant was observed of 0.084 min^{-1} using medium pressure UV light (Hansen et al.

2013). These results indicated that even with the presence of three bonds of C-Cl in CH, the photodegradation was fast under UV irradiation, and that could be attributed to the presence of acetaldehyde side group that may weakens C-X bonds leading to higher losses (Chuang et al. 2016).

1.4.3 Haloacetonitriles, Halonitromethanes and Nitrosamines

Several studies investigated the stability of the highly carcinogenic nitrogenous haloacetonitriles (HANs), halonitromethanes (HNMs) and nitrosamines (NAs) by photolysis. Medium pressure UV irradiation on HANs showed significant photodegradation of dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN) and trichloroacetonitrile (TCAN) with rate constants of 0.024, 0.094, 0.2 and 0.130 min^{-1}, respectively (Hansen et al. 2013). The results showed that DCAN was the most recalcitrant to be removed in contrast with the other HANs, where replacing chlorine with bromine atom increased the photolytic decay. Another photolysis study on HANs compared degradation rates by UV 254 nm alone and vacuum UV (185 +254 nm). The results showed first order rate constants for monochloroacetonitrile (MCAN), DCAN, TCAN and DBAN were 2-7 times higher than UV254 photolysis alone. However, the degradation order efficiency did not change where MCAN < DCAN < TCAN < DBAN and degradation increased with increase in halogen atom numbers (tri > di > mono) and type of substituted halogen associated with DBP (I > Br > Cl) (Kiattisaksiri et al. 2016). Similar results were also observed by different UV photolysis studies (Hou et al. 2017, Ling et al. 2016, Yin et al. 2018, Zhang et al. 2019b). However, by solar photolysis, Lekkas and Nikolaou 2004 observed spiked in MCAN concentrations where DCAN was subjected to some photolytic losses.

Additionally, BCAN, DBAN and DCAN underwent photolytic degradation at first order rate constants of 0.329, 0.324 and 0.063 h^{-1}, respectively under sunlight irradiation (Chen et al. 2010). These findings suggest that direct photolysis process (UV or sunlight) is not major degradation mechanism for chlorinated HANs but effective on brominated HANs, due to the presence of C-Cl bonds that require higher energy than C-Br to break. Moreover, C≡N bonds present in acetonitrile side group require 866 kJ mol^{-1} to break (Bertini et al. 1994), which is higher than photon energy in UV wavelengths used in the previous studies, making it difficult to breakdown and thus increase total HANs stability (Chuang et al. 2016).

Halonitromethanes (HNMs) are group of toxic nitrogenous DBPs found in drinking water and wastewater (Krasner et al. 2006, Krasner et al. 2009) including trichloronitromethane (chloropicrin, TCNM), bromodichloronitromethane (BDCNM), chlorodibromonitromethane (CDBNM), tribromonitromethane (bromopicrin, TBNM), dichloronitromethane (DCNM), bromochloronitromethane (BCNM), dibromonitromethane (DBNM), chloronitromethane (CNM), and bromonitromethane (BNM). UV Photolysis at 254 nm of HNMs species were conducted on TCNM, DCNM, DBNM and BNM at pH 3-9. Results concluded high stability of all species at acidic pH, where TCNM was stable at all pH tested. However, at alkaline pH, HNMs photodegradation increased and showed sharp increase at pH near their pKa values. These findings indicate that at high pH values, deprotonated structures of HNMs tend to increase UV absorption, thus may lead to higher degradation rate in comparison with acidic pHs (Fang et al. 2013). These results contradicted with another study where TCNM showed significant photodegradation at natural pH and 26 °C using medium

pressure UV light, where the rate constant was 0.523 min^{-1} (Hansen et al. 2013). However, under natural sunlight, Chen et al. 2010 reported degradation rate constants of 0.09 to 0.8 h^{-1} for five HNMs tested, where degradation increase with number of halogen and bromination degree. Additionally, TCNM showed first order rate constant of 0.504 h^{-1} under natural sunlight (Castro and Belser 1981). Several studies also investigated TCNM photodegradation in gaseous conditions under sunlight or UV irradiation. A study by Wade et al. 2015 on TCNM photodegradation in atmosphere reported half-life of 5.9 h by simulated sunlight, which agreed with other studies (Allston et al. 1978b, Vera et al. 2010). However, using UV light resulted in higher photolytic rates with half-life of 14 ~ 300 min when 190 - 400 nm used (Allston et al. 1978a, Wade et al. 2002). In general, these findings indicate that TCNM can be rapidly photolyzed by either sunlight or UV irradiation. HNMs photodegradation pathways are based upon pH, where at acidic pH homolysis is likely to be the major photolysis pathway for all four HNMs to produce halides, nitrite and nitrate. However, at higher pHs, heterolysis possibly the dominant pathway for the formation of carbon dioxide, nitrite and halides as major products for di-HNMs, and the formation of nitrite, halides and other unknown organics for mono-HNMs (Chuang et al. 2016, Fang et al. 2013).

Nitrosamines (NAs) are known toxic nitrogenous DBPs that have been found in drinking and surface water including N-nitrosodimethylamine (NDMA), N-nitrosomethylethylamine (NMEA), N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), N-nitrosodibutylamine (NDBA), N-nitrosomorpholine (NMOR), N-nitrosopyrrolidine (NPYR) and N-nitrosopiperidine (NPIP). Several studies examined NAs stability by photolysis processes. All eight NAs were rapidly photolyzed

under sunlight irradiation (~1300 W/m^2) where half-lives ranged between 8 to 10 min (rate constants around 4.9 h^{-1}). The photodegradation rates of NAs were based upon the side group associated with the NA. Cyclic-carbon chain NAs were photolyzed faster than methyl and/or ethyl side group NAs (Chen et al. 2010). This also agreed with another study where NAs were reported half-lives of 12 to 16 min under simulated sunlight (765 W/m^2) (Plumlee et al. 2007). NAs were also photosensitive to UV irradiation at 253.7 nm. All NAs were decomposed within the first 10 min of photodegradation using 4W, low pressure Hg lamp (Afzal et al. 2016). Between all NAs, NDMA was specifically investigated in the literature due to its higher toxicity and occurrence in drinking and surface water (Krasner et al. 2013, Mitch et al. 2003). NDMA was reported to be photosensitive at two different wavelengths including 228 and 332 nm (Stefan and Bolton 2002). Regardless of any wavelength used, degradation started by cleavage of N-N bond upon irradiation forming nitrogenous reactive radical (NO•) that continuously increase NDMA photodegradation. Two different pathways have been proposed for NDMA photodegradation. The pathways strongly depend on NDMA initial concentration and solution pH (Aqeel et al. 2017, Lee et al. 2005b). The most known pathways happen at higher NDMA concentrations and low pH (3-5). An excited state of NDMA formed N-nitrosodimethylammonium ion, that quickly hydrolyzed forming dimethylaminium (DMA), acids and nitrite ion (NO_2^-) as final products. Where the other pathway was similar to hydrolysis (Lee et al. 2005a, Lee et al. 2005b). Regardless of pathway, final or intermediate products are safe products, therefore, photolysis is an important mechanism that can be utilized for NAs degradation to protect water.

1.4.4 Emerging DBPs

Several groups of new DBPs have been recently identified in chlorinated waste and drinking waters rich in bromide and iodide ions. Some of these DBPs are several times more toxic than regulated THMs and HAAs including halophenolics, halobenzoquinones (HBQs), chlorophenylacetonitriles (CPANs), trihalo-hydroxy-cyclopentene-diones (trihalo-HCDs) and iodo-related DBPs (Gong and Zhang 2015, Li et al. 2015, Pan et al. 2016, Plewa et al. 2004, Sun et al. 2019, Zhang et al. 2019a, Zhang et al. 2018b). Photolysis studies on these DBPs have been very limited in the literature. A study by Qian examined the stability of HBQs under UV254 irradiation. HBQs tested were 2,6-dichloro-1,4-benzoquinone (DCBQ), 2,3,6-trichloro-1,4-benzoquinone (TCBQ), 2,6-dichloro-3-methyl-1,4-benzoquinone (DCMBQ), and 2,6-dichloro-1,4-benzoquinone (DBBQ). The results concluded that these DBPs may convert to OH-HBQs that subsequently dissociate to monohalogenated benzoquinones as end products, however further investigation is required to understand whether they pose a health risk (Qian et al. 2013). Zhang group investigated the photodegradation of 21 halophenolic DBPs including 5-bromosalicylic acid, ,5-dibromohydroquinone, 2,4,6-triiodophenol and others under sunlight irradiation at sea water. The degradation initiated by photoconversion triggered by photonucleophilic substitution, where bromo- and iodo-phenolic species converted to their chlorophenolic and hydroxyphenolic analogues. Afterwards, chlorophenolic DBPs converted to their hydroxyphenolic analogues. The formed hydroxyphenolic DBPs undergo more decomposition forming aliphatic compounds as end products. The half-life ranged between 1.5 to 353.1 h, where iodophenolic DBPs were faster in degradation than their bromophenolic, which in turn faster than their chlorophenolic counterparts (Liu et al. 2016, Liu et al. 2019). More research is still

needed to investigate the stability of the other new emerging DBPs by photolysis processes to identify their presence and fate in receiving waters.

1.4.5 Summary

- Photolysis processes including the use of solar or artificial light showed various degradation results of carbonaceous and nitrogenous DBPs in water
- Generally, carbonaceous DBPs including THMs, HAAs, HKs and haloacetaldehydes showed high resistance to solar and UV photolysis. However, nitrogenous DBPs including HNMs, HANs and NAs were more photodegradable, and the rankings were as follow: NAs > HNMs > HANs.
- Photodegradation rates of DBPs increased based on substituted halogen associated with the DBP as follow: I-DBPs > Br-DBPs > Cl-DBPs.
- Photodegradation rates of DBPs increased based on the number of halogens in the DBP where: trihalo-DBPs > dihalo-DBPs > monohalo-DBPs.
- Photodegradation mechanism of DBPs is mainly dehalogenation, where C-I bond is photolytic than C-Br and C-Cl. This is due to the dissociation energy required to break the carbon-halogen bonds: 397, 280, 209 kJ/mol for C-Cl, C-Br, and C-I, respectively.
- The steric and electronic effects of halogen substituents may also play an important role in the photosensitive cleavage of carbon-halogen bonds. DBPs with higher numbers of halogen atoms exhibited higher photolytic dehalogenation degrees, which can be attributed to the increased electron withdrawing effects.

- Using UV irradiation for DBPs degradation tended to increase photosensitivity of the compounds, resulting in higher photodegradation rates in comparison to sunlight.
- Photodegradation of the new emerging DBPs may lead to the formation of intermediates that more toxic than the parent compounds.

1.5 Research Gaps

A summary of literature review identified several key research gaps for DBPs photolysis in water as follows:

1. Traditional DBPs photolysis studies have only investigated the fate of individual chlorinated, brominated and iodinated DBPs including THMs, HAAs and others by natural sunlight in surface water. However, TOCl, TOBr and TOI have not been examined. TOX formed in wastewater effluent is discharged to drinking water supplies accounts for all halogenated DBPs including the unknown DBPs that may pose health hazards to the public and marine life.
2. DBPs photodegradation studies have not examined the complete dehalogenation of DBPs in water that lead to the formation of safe end-products including water, carbon dioxide and halide acids. The studies only investigated the disappearance of the parent DBP compound without identifying the possible formation of intermediates compounds that could be more toxic than the parent compound.
3. Several groups of the new emerging DBPs including haloacetamides and iodinated DBPs that present in receiving waters have not yet been

investigated by photolysis processes. These emerging DBPs have been reported to be several times more toxic than the regulated THMs and HAAs.

4. There is a lack of research investigating the applicability of eliminating DBPs from wastewater effluent prior to discharge into drinking water supplies using advanced oxidation processes that utilize natural sunlight for oxidative radical formation to break DBPs in water.

1.6 Research Objectives

The objectives of this dissertation are to 1) Evaluate the impact of sample preservation techniques on the stability of TOCl, TOBr and TOI in water; 2) Determine the fate of TOCl, TOBr, TOI and individual DBPs in surface water under natural solar photolysis; and 3) Investigate the removal of chlorinated, brominated and iodinated DBPs by advanced oxidation processes including natural solar photocatalytic process by TiO_2 and natural solar photo-fenton process.

1.7 Research Hypotheses

1. TOI is more photosensitive compared to TOBr which is more photosensitive than TOCl under exposure to natural sunlight.
2. Natural solar photodegradation of individual DBPs are based on the association with the side group, number of halogens and size of substituted halogen in each DBP
3. Advanced oxidation processes including solar photo-fenton, photocatalysis by TiO2, ultraviolet (UV)/hydrogen peroxide (H_2O_2) and others induce DBPs

degradation and reduce half-lives from days and hours to minutes and seconds.

4. Natural contaminants that exist in treated wastewater and surface water reduce DBPs degradation by natural sunlight and advanced oxidation processes.

1.8 Dissertation Layout

The first part of this study examined the proper procedure to be followed to maintain stable TOX concentrations during sample storage. Various factors have been considered including the impact of storage temperature, holding time, type and concentration of quenching agents and acidification. The results are presented in chapter two “Evaluation of Sample Preservation Techniques to Improve Total Organic Halogen Analysis” The outcome of this study improved TOX recovery and thus the new procedure was followed throughout the other experiments presented in this dissertation.

The second study investigated the fate of TOCl, TOBr and TOI in water by natural solar photolysis. Furthermore, the study determined kinetics and half-lives for each TOX and UTOX at different pHs, and the impact of natural water contaminants on TOX photodegradation rates. The results are presented in chapter three “Natural Solar Photolysis of Total Organic Chlorine, Bromine and Iodine in Water”.

The third study examined the impact of natural sunlight on the photodehalogenation of individual chlorinated, brominated and iodinated DBPs in water including THMs, HAAs, HANs, HAs, HNMs and haloacetamides. The study also examined the impact of natural water contaminants including nitrate, nitrite and NOM on

DBPs photogeneration rates by solar photolysis. The results are presented in chapter four "Photolytic Dehalogenation of Disinfection Byproducts in Water by Natural Sunlight Irradiation"

The fourth study examined the application of natural solar photocatalytic process with added TiO_2 on the removal of TOCl, TOBr and TOI in water. The study determined the optimal conditions must be utilized to achieve highest TOX removal, including TiO_2 dose and phase, pH and photolysis time. Moreover, kinetics was determined for TOX species photocatalytic degradation in drinking water and wastewater effluents under natural sunlight. The results are presented in chapter five "Photocatalytic Degradation of Disinfection Byproducts Using Natural Sunlight and TiO_2".

The final study investigated the use of natural solar photo-fenton process on the degradation of TOCl, TOBr, TOI and individual DBPs in water at neutral pH. Operational conditions were monitored during the experiment including dissolved organic carbon, hydrogen peroxide, pH and iron. In addition, the impacts of natural water contaminants (sulfate, chloride, NOM, nitrate) on DBPs degradation rates were evaluated. The results are presented in chapter six "Disinfection Byproducts Removal Using Natural Solar Photo-Fenton".

Chapter seven summarizes the key findings, conclusions and identify future research needs.

Table 1.1: DBPs regulations and guidelines

Regulated DBPs	Maximum Contamination Level MCL (mg/L)
U.S. Environmental Protection Agency (EPA) regulations	
Total THMs (4THMs)	0.08
Total HAAs (5HAAs)	0.06
Bromate	0.01
Chlorite	0.1
World Health Organization (WHO) regulations	
Chloroform ($CHCl_3$)	0.3
Bromoform ($CHBr_3$)	0.1
Bromodichloromethane ($CHBrCl_2$)	0.06
Chlorodibromomethane ($CHClBr_2$)	0.1
Chloroacetic acid ($CH_3ClCOOH$)	0.02
Dichloroacetic acid (CH_2Cl_2COOH)	0.05
Trichloroacetic acid ($CHCl_3COOH$)	0.2
Bromate	0.01
Chlorite	0.7
Dichloroacetonitrile	0.02
Dibromoacetonitrile	0.07
2,4,6-trichlorophenol	0.2
N-Nitrosodimethylamine (NMDA)	0.1
Bromate	0.01
European Union Standards	
Total THMs (4THMs)	0.1

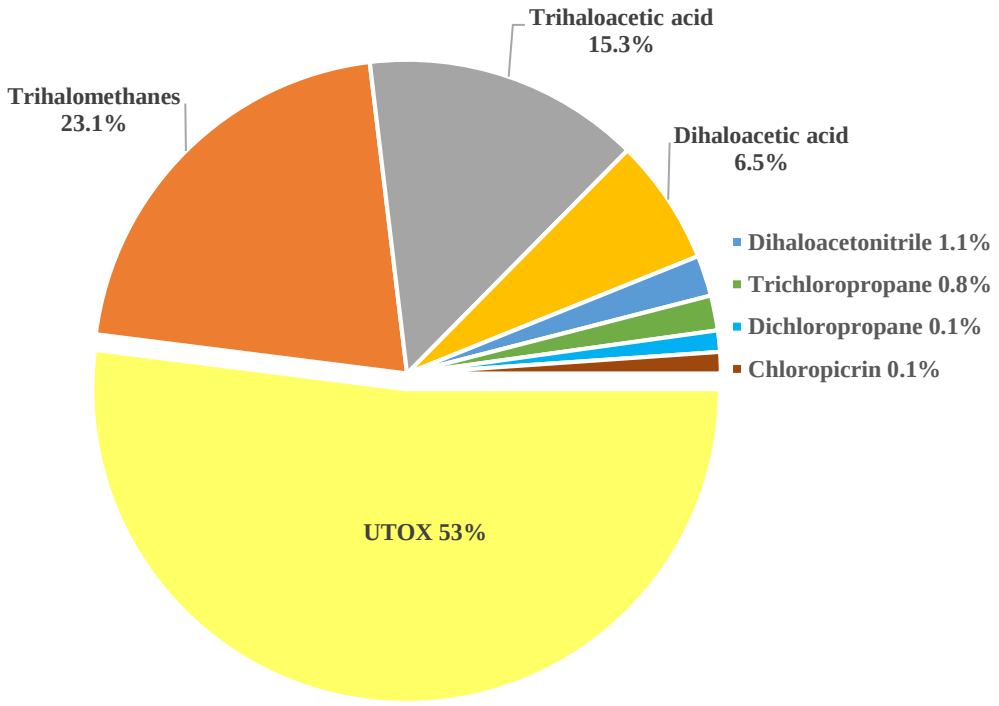

Figure 1.1: TOX distribution in chlorinated water

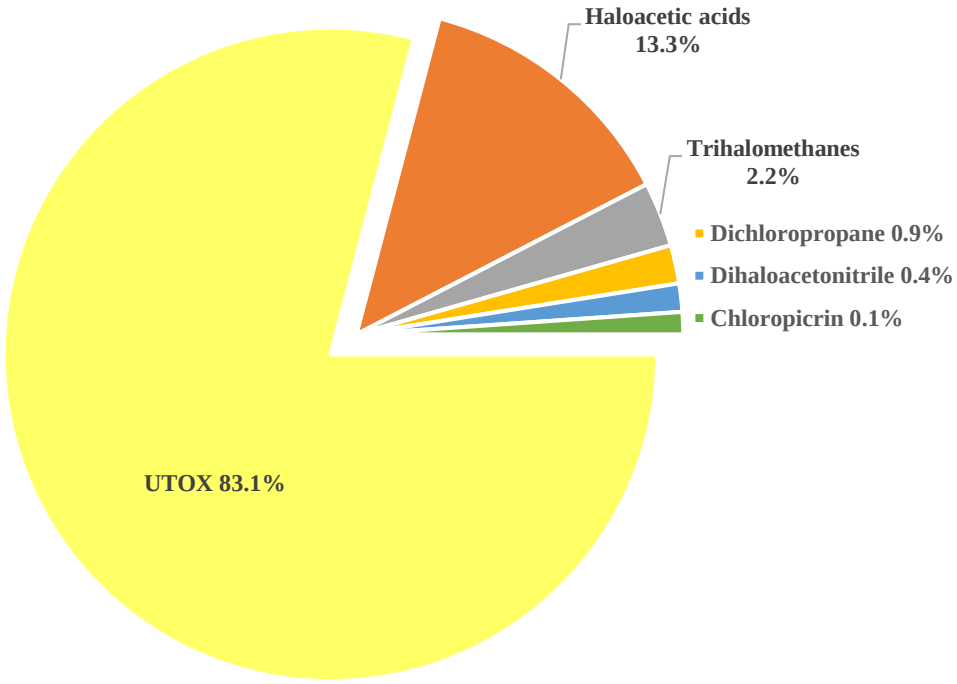

Figure 1.2: TOX distribution in chloraminated water

CHAPTER TWO
EVALUATION OF SAMPLE PRESERVATION TECHNIQUES TO IMPROVE TOTAL ORGANIC HALOGEN ANALYSIS

Abstract

The goal of this study was to determine the optimum sample preservation conditions to stabilize total organic halogen (TOX) concentrations in water during storage. TOX was differentiated to total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI) and measured using a TOX analyzer following adsorption-pyrolysis-titration protocol. The study examined TOX recovery under the impact of different sample temperatures and nitrate wash volumes during the activated carbon adsorption step. Furthermore, TOX concentrations were monitored in the presence of quenching agents (sodium sulfite, sodium thiosulfate and ascorbic acid) at acidic pH (sulfuric, phosphoric, nitric acid) to determine the optimum quenching agent and concentration to maintain stable TOX during holding time at low temperatures. Results showed that lower sample temperatures (4 °C) and lower nitrate wash volume (15 mL of 1000 mg NO_3^-/L) are the ideal conditions to increase TOX recovery. No universal quenching agent was found to maintain stable TOX concentrations during storage, however, reserving TOX at acidic pH (≤ 2) reduced the impact of quenching agents. Overdosing of any quenching agents (≥ 1000 μM) severely degraded TOX regardless of holding time and storing pH conditions. Sulfuric and phosphoric acids must be avoided for TOI analysis when dropping pH, since it produced contamination leading to false TOX measurement.

2.1 Introduction

To protect the public health from waterborne diseases in drinking water, disinfection practice has been widely used to deactivate the causing-diseases microorganisms by adding oxidants including chlorine (Cl_2), monochloramine (NH_2Cl), chlorine dioxide (ClO_2) or others. However, as one unintended side effect of disinfection is the reaction with naturally existing organic materials (NOM) in water, leading to the formation of toxic byproducts identified as disinfection byproducts (DBPs) (Krasner et al. 2009). Due to the presence of bromide and iodide ions in natural waters, chlorine can also oxidize these ions leading to the formation of brominated and iodinated DBPs, that have been reported to be more carcinogenic and genotoxic than their chlorinated analogues (Duirk et al. 2011, Parker et al. 2014). As a reaction, US environmental protection agency (EPA) has regulated multiple groups of DBPs in drinking water in an effort to reduce their associated health risks to public life.

Halogenated DBPs can be identified and quantified individually such as trihalomethanes (THMs), haloacetic acids (HAAs), haloketones (HKs), haloacetonitriles (HANs), haloacetamides (HAMs) and others, or quantified as total halogenated concentration using total organic halogen (TOX) parameter regardless of their identification. TOX provides an attractive alternative for measurement of individual known DBPs, however, many studies reported that these DBPs account for only 50% in chlorinated drinking water, where in chloraminated water, about 20% of total TOX measured (Hua and Reckhow 2008a). Therefore, TOX was capable of measuring a new fraction of unknown DBPs that were not identified by common analytical methods, which is known in literature as unknown TOX (UTOX). This UTOX may contain many

toxic DBPs that may cause health issues for public (Richardson et al. 2007). Therefore, TOX has been considered as master parameter and indicator for DBPs toxicity in water (Liu and Zhang 2013).

TOX can be measured using adsorption-pyrolysis-titration technique following 5340B in Standard Methods (Rice et al. 2017). The method recommends that prior an analysis, TOX samples should be stored in 4 °C refrigerator at pH ≤ 2, and if chlorine residual is present, it must be quenched using sodium sulfite followed by sulfuric (H_2SO_4) or nitric acid (HNO_3) to prevent continuing formation of halogenated compounds during the holding time. However, samples should be analyzed within 14 days. Afterwards, TOX determined in two steps 1) concentrating halogenated compounds into activated carbon (AC) by adsorption, and the interference from inorganic halides can be flushed out by nitrate ions competitive displacement 2) transferring AC samples to the pyrolysis and titration processes for total halide measurement.

It has been widely investigated that TOX sample preservation protocol including the use of quenching agents, holding time, sample pH and AC adsorption can negatively impact individual DBPs stability (Hua and Reckhow 2006, Kristiana et al. 2014). However, its impacts in total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI) formed by NOM have not been addressed thoroughly in literature. A study by Liu and Zhang showed that using arsenite ($NaAsO_2$) as quenching agent in TOCl and TOBr samples, can decrease TOX recoveries after 60 min of quenching time, due to competitive adsorption by arsenite on AC and decomposition of TOX by excessive arsenite (Liu and Zhang 2013). Additionally, an earlier study by the authors concluded that TOX stability decreased in the order of: TOI > TOBr > TOCl under alkaline pH

conditions (Hua and Reckhow 2012). These studies examined few TOX sample preservation techniques and demonstrated significant changes in TOX concentrations, suggesting that TOX analytical approach is unverified. Therefore, further investigations are still needed to improve the overall TOX measurement accuracy especially regarding TOBr and TOI.

The objective of this study is to examine the key parameters that can affect TOX recoveries during sample preservation and AC adsorption techniques. These parameters include the impact of quenching agents, quenching time, acidification, sample temperature and nitrate wash on TOCl, TOBr and TOI formed by NOM. The outcome of this paper should help environmental researchers and water treatment professionals to better control all halogenated DBPs by determining the optimum sample preservation and AC adsorption conditions that will increase TOX recoveries during analysis.

2.2 Materials and methods

2.2.1 Chemicals

Chlorine, bromine and iodine stocks were prepared by dissolving sodium hypochlorite solution (NaOCl 5.65-6% Fisher Scientific), bromine solution (>99.5%, Sigma Aldrich, St Luis, MO), and solid iodine (>99.8%, Sigma Aldrich) in water, respectively. Monochloramine stock was made onsite by mixing sodium hypochlorite solution and soluble ammonium sulfate at Cl_2:N ratio of 0.8:1. Prior to mixing, the pH for the solutions were adjusted to 8.5 using either sodium hydroxide or H_2SO_4. Suwannee river fulvic acid (SRFA) was obtained from the International Humic Substances Society. All DBPs used in this study were purchased from Sigma Aldrich (St Luis, MO NJ) unless otherwise noted. DBPs included; three THMs (chloroform, bromoform, iodoform), nine

HAAs (monochloro-, monobromo-, monoiodo-, dichloro-, dibromo-, diiodo-, trichloro-, tribromo-, and triiodoacetic acid (MCAA, MBAA, MIAA, DCAA, DBAA, DIAA, TCAA, TBAA, and TIAA, respectively)), two HANs (dichloro- and dibromoacetonitrile (DCAN, and DBAN)), trichloronitromethane (TCNM), chloral hydrate (CH), and dichloroacetamide (DCAcAm). DIAA (90%), and TIAA (90%) were obtained from Toronto Research Chemicals, Inc. (Toronto, Ontario). All DBPs were analytical grade purity. Quenching agents used were sodium sulfite (Na_2SO_3, 98.6% Fisher Scientific, NJ), sodium thiosulfate ($Na_2S_2O_3$) and ascorbic acid ($C_6H_8O_6$, 99% Acros Organics, NJ). Additionally, three types of different acids were used including sulfuric acid (H_2SO_4), nitric acid (HNO_3) and phosphoric acid (H_3PO_4).

2.2.2 Preparation of TOX and DBP sample

A concentration of 3.0 mg Cl_2/L, 0.4 mg Cl_2/L, 2.0 mg Br_2/L and 1.0 mg I_2/L of chlorine, monochloramine, bromine and iodine were dosed to four different sets of dissolved organic carbon (DOC) solutions to produce TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI, respectively. DOC solutions were made by dissolving SRFA in water at concentration of 3.0 mg C/L. The oxidation experiments were conducted in 300 mL chlorine-demand free bottles at pH 7.0 ± 0.1 using 1 M phosphate buffer. Afterwards, samples were placed in 20 °C incubator for 72-h to allow for complete consumption of oxidants with no residual left at the end of incubation period. The specific concentrations of the oxidants used in this study to produce TOX were selected based on two factors; to present typical disinfectant concentrations practiced in water and wastewater treatment plants and to produce large amounts of TOX for better quantification during analysis.

Individual DBPs were prepared separately by using aliquots from standard stocks at initial concentration of 200 µg/L as Cl, Br, or I for chlorinated, brominated, and iodinated DBPs, respectively. The samples were buffered using 1 M phosphate to set the pH to 7.0 ± 0.1. All DBPs were dissolved in water except for bromoform, chloroform, DBAN, DCAN, iodoform, and TCNM dissolved in acetone, since they have low solubility in water. All solutions in this study were prepared using ultrapure water (18 MΩ-cm, Barnstead NANOpure system).

2.2.3 Experimental Approach

In this study, two sets of experiments were conducted to address the impact of sample preservation on TOX concentrations. The first experiment investigated the impact of sample storage temperature and nitrate wash volume on TOX and DBPs recoveries during the AC adsorption process. Samples were stored in three different temperatures (4, 10, 20 °C) at pH 7.0 for 6 hr to cover a wide range of possible storage scenarios. Afterwards, the pH was adjusted to 2 using nitric acid immediately prior to the AC adsorption. After adsorption, AC samples were washed with potassium nitrate solution (1000 mg/L as NO_3) using 10, 15, 25, 35 and 50 mL.

The second experiment addressed the impact of using quenching and/or acids agents on TOX stability during sample storage. Quenching impact on TOX during storage was examined by using different quenching agents including sodium sulfite, sodium thiosulfate and ascorbic acid at different concentrations of 40, 200 and 1000 mM and quenching time of 0, 1, 6, 12, 24, 72, 168 and 336 hr. TOX samples were dosed with the appropriate quenching agent and then stored at 4 °C for the assigned period. Then, pH for the samples was adjusted to 2 using nitric acid and directly subjected to the AC

adsorption. The impact of acidification on TOX during storage was evaluated by comparing the use of different acids including sulfuric, phosphoric and nitric acid to adjust TOX samples pH to 2 and then store the samples for 14 days at 4 °C prior to TOX measurement. After the 14 days, samples immediately went through the AC adsorption process for further TOX analysis. It's important to mention that during this study, TOX and DBPs samples were not dosed with any additional oxidants or contained any oxidants residual prior to dosing the appropriate quenching or/and acid agents.

2.2.4 Analytical Approach

TOX concentrations were detected using TOX-100 analyzer from Mitsubishi (Cosa Xentaur Inc., Norwood, NJ). The details about the detection are given in the next section. Oxidants including chlorine, monochloramine, bromine and iodine were analyzed using DPD ferrous titrimetric method. Detection of DOC was conducted via TOC analyzer-5000 by Shimadzu following Standard Method 5310B. Chloride, bromide and iodide ions were measured using ion chromatography (DX-500) equipped with conductivity detector (CD-20) from Dionex.

2.4.1 Detection of TOX by adsorption-pyrolysis-titration method

Analysis of TOX was conducted following the standard method 5340B with minor changes. Briefly, samples (130 mL) were acidified to pH 2 using nitric acid and then 40 mL adsorbed into two prepacked AC columns (TOX-100 Calgon Carbon, Mitsubishi) at 3.3 mL/min flowrate using three channel adsorption module model (TX3AA, Mitsubishi). Afterwards, the AC columns were washed with 15 mL of 1000 mg/L as NO_3^- to remove inorganic halides and then placed in quartz sample boat at the automatic boat controller (TX-3BC, Mitsubishi). The 15 mL nitrate wash volume was

selected based on the results demonstrated on Table 2.2 where different wash volumes were tested, and 15 mL showed the highest removal of inorganic halides with highest TOX recovery. The details are demonstrated in the next section.

After the nitrate wash, AC samples were introduced to pyrolysis at 900 °C electrical furnace (TOX-100, Mitsubishi) in presence of oxygen (O_2). The generated hydrogen halides and other gases were carried via Argon (Ar)/O_2 and passed through dehydrating tube (TX2BAS, Mitsubishi) filled with 10 mL of concentrated sulfuric acid to remove water vapor. The O_2 and Ar/O_2 flow rates were set at 150 and 200 mL/min during the analysis. After the elimination of water vapor, gas was transferred to the acetic acid titration cell via transfer line for TOX detection. TOX was expressed as TOX specific-halogen because pure oxidants were used to produce TOX from SRFA solutions. Additionally, SRFA solution, AC, quartz boat and ultrapure water were measured for TOX contaminations. Results showed low TOX contamination was detected for SRFA solution and for the AC used in this study, with average background of 2.5 and 2.2 µg Cl_2/L, respectively, where ultrapure water and quartz boat (pre-baked) have not been detected for any TOX. Therefore, the background contaminations have been subtracted from TOCl sample concentrations since its essential for accuracy.

The precision of the TOX specific-halogen method was assessed by measuring individual chlorinated, brominated and iodinated DBPs recovery including TCAA, DCAA, MCAA, TBAA, DBAA, MBAA, TIAA, DIAA, MIAA, Chloroform, Bromofrom, Iodoform, DCAN, DBAN, DCAcAm, CH and TCNM. DBPs were stored in 4, 10 and 20 °C incubators for 6 h and afterwards directly subjected to AC adsorption and

nitrate wash before TOX analysis. The recovery averaged between 98 and 102% for all tested DBPs and the results are presented in Table 2.1.

2.3 Results and discussion

2.3.1 Impact of Nitrate Wash Volumes on TOX Recovery

Nitrate wash is a critical step in TOX analysis, since it removes inorganic halides from AC samples that interfere with TOX measurement during titration. Table 2.2 presents the impact of using different nitrate wash volumes on TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI concentrations. Results show that higher wash volume used, the lower TOX concentration recovered. TOX decreased by < 5% when 20 mL used in contrast with 10 mL. However, when TOX was washed with 50 mL, values decreased by 13.9, 14.2, 18.7 and 31% for TOCl (Cl_2), TOBr, TOI and TOCl (NH_2Cl), respectively. The observed TOX decrease when 50 mL was used, was also incorporated with a shift in majority of TOX concentrated in the second AC column rather than the first. Fig 2.1 demonstrate the impact of using different nitrate wash volume on TOX recovery at the second AC column to total concentration. Results showed that when 10 mL used, second column absorbed 18.2, 23.1, 29.3 and 45.2% of total TOCl (Cl_2), TOBr, TOI and TOCl (NH_2Cl) concentrations, respectively. However, at 50 mL, recovery at second column increased to 43.8, 45.8, 63.8 and 71.3%. Results from Table 2.2 and Fig 2.1 clearly indicated that nitrate wash volume has significant impact on TOX concentration and recovery. More caution needs to be considered particularly for TOCl (NH_2Cl) and TOI, since their concentrations have been decreased the most when flushed with higher nitrate wash volumes and mostly recovered in second column rather than first. This indicates that TOCl (NH_2Cl) and TOI contain significant portions of halogenated organic compounds that have weak adsorption bonds with activated carbon, therefore can be

flushed significantly easier than TOCl (Cl_2) and TOBr compounds. For example, the authors previously examined the impact of nitrate wash volumes on DCAA using 1240 mg/L NO_3^-at pH using nitric acid. Only 78% of was recovered when DCAA samples were rinsed with 30 mL wash volume (Hua and Reckhow 2006). DCAA contribute to about 20% of TOCl (NH_2Cl), consequently, this agrees with this study results. Moreover, the additional lower recovery measured in this study might be attributed by the unknown fraction of TOX that could have lower adsorption capabilities on AC surfaces (Kristiana et al. 2015). Therefore, more research is needed to investigate the recovery of UTOX fraction by different nitrate wash rinse volumes.

The order of TOX reduction and increase in ratio of second AC column recovery increased as follow: TOCl (NH_2Cl) > TOI > TOBr > TOCl (Cl_2) with an increase in nitrate wash volume. Therefore, to avoid the impact of larger amounts of nitrate wash in this study, ≥ 20 mL wash volume was avoided and 15 mL was used for further TOX analysis using 1000 mg/L NO_3^- stock at pH 2 by nitric acid. 15 mL has no significant impact on TOX concentrations and recoveries in second column in comparison to when 10 mL was operated. Additionally, it should be adequate for removing interferences from inorganic halides. In earlier study by the authors, 15 mL of nitrate wash volume using 1000 mg/L NO_3 stock (pH =2 by nitric acid) was capable of completely flushing 1000 mg/L of chloride (Hua and Reckhow 2006). Thus, as long as less than 1000 mg Cl^-/L is used, 15 mL should be ideal for TOX measurement.

2.3.2 Impact of Sample Preservation Temperature on TOX and DBPs Recovery

TOX and DBP samples were stored in different temperatures including 4°, 10° and 20 °C at pH 2 using nitric acid for a 6 h period, to examine the temperature impact on halogenated compound adsorption by AC during TOX analysis. These temperatures were selected to cover a wide range of possible sample storing temperature before TOX measurement. After 6 h of storage, samples were subjected to AC adsorption and then rinsed with 15 mL of nitrate solution (1000 mg/L NO_3^-, pH 2 by nitric acid). The results for TOX species were presented at Fig 2.2 and it showed decrease in TOX recovery when temperature increased. At 20 °C TOX concentrations decreased by 5.1, 6.8, 7.4 and 8.4% in comparison with 4 °C for TOCl (Cl_2), TOBr, TOI and TOCl (NH_2Cl), respectively. Furthermore, the second AC column showed an increase in TOX concentration at higher temperatures rather than the first column for all four TOX species. TOCl (Cl_2) and TOBr showed an average of 6.3% increase in TOX at 20 °C and 11.5% for TOCl (NH_2Cl) and TOI. This indicate that higher temperatures can decrease the reactivity of halogenated compounds with the AC surface, leading to increase recovery at the second AC column and decrease TOX overall recovery. The results also indicated that TOCl (NH_2Cl) and TOI were more susceptible to temperature changes than TOCl (Cl_2) and TOBr and the order of reduction increase as follows: TOCl (NH_2Cl) > TOI > TOBr > TOCl (Cl_2). On the other hand, individual DBPs recoveries were also investigated under the impact of temperature changes and the results are presented in Table 2.1. Surprisingly, all DBPs did not show any significant impact under any temperature and the recovery averaged between 98 and 102% and this agrees with other recent studies (Abusallout and Hua 2016a, b, Gong and Zhang 2013, Kristiana et al. 2015, Langsa et al. 2017, Li et al. 2011).

Therefore, the significant impact observed on TOX can be attributed to the nature of the UTOX that might contain halogenated organic species that are not very adhesive to AC surfaces at higher temperatures and can be flushed easier in contrast with the known fraction of TOX. To avoid any unnecessary impact of temperature on subsequent experiments, samples were analyzed at 4 °C during AC adsorption and rinsed with 15 mL of nitrate solution (1000 mg/L NO_3^-) for all tested TOX and DBP samples unless otherwise stated. The resulting control TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI concentrations for all experiments were 534 ± 13 µg Cl_2/L, 102 ± 5 µg Cl_2/L, 470 ± 10 µg Br_2/L and 334 ± 7 µg I_2/L, respectively.

2.3.3 Impact of Quenching Agents on TOX Stability

Table 2.3 demonstrates the impact of using quenching agents on TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI recoveries. TOX samples were quenched with sodium sulfite, sodium thiosulfate or ascorbic acid at different concentrations including 40, 200 and 1000 µM at pH 7. Then stored at 4 °C refrigerator for 336 h (14 days) for further TOX analysis. TOX samples did not contain any oxidant residual prior to quenching, to determine the impact of actual quenching agent concentrations on TOX recoveries. Results demonstrated that TOX samples with no quenching agents added showed degradation rates of 6.6, 8.4, 13.7 and 16.5% for TOCl (Cl_2), TOBr, TOI and TOCl (NH_2Cl) after 14 day of holding time at 4 °C and pH 7 due to hydrolysis (Abusallout et al. 2017). Furthermore, results showed that regardless of the quenching agent or concentration used, all four TOX species recoveries were even lower than TOX samples with no quenching agents. Thus, the use of quenching agents for TOX species should be carefully monitored when used. However, TOX was least impacted at 40 µM in contrast

to the higher concentrations. When 1000 µM used, recoveries averaged 82.9, 70.9, 46.6 and 29.9% for TOCl (Cl_2), TOBr, TOCl (NH_2Cl) and TOI, respectively, but when 40 µM applied, recoveries increased to 90, 83.4, 73.4 and 71.2%. Therefore, overdosing of any quenching agent must be avoided when preserving TOX samples at low temperatures. Additionally, results indicated that in the presence of the same quenching agent type and concentration, TOX species behaved differently where the stability decreased in the following order: TOI > TOCl (NH_2Cl) > TOBr > TOCl (Cl_2).

To further analyze the impact of quenching agents on TOX stability at 4 °C and pH 7, samples at 200 µM were stored at different quenching times to determine the order of degradation and suitable quenching agent for better TOX preservation. Results presented in Fig 2.3 demonstrated that TOX degradation by 200 µM of sodium sulfite, sodium thiosulfate and ascorbic acid followed first order kinetics, where half-lives ranged between 65.3-80.6, 42.9-56.4, 25.3-34.7 and 13.5-22.7 days for TOCl (Cl_2), TOBr, TOCl (NH_2Cl) and TOI, respectively. Results also demonstrated that sodium sulfite was the most suitable quenching agent for preserving chlorinated compounds including TOCl (Cl_2) and TOCl (NH_2Cl), where for TOBr, thiosulfate showed the highest TOX recovery. On the contrary, TOCl (Cl_2), TOBr, and TOCl (NH_2Cl) showed the least recovery when ascorbic acid was present. However, when used for quenching TOI, results showed the highest recovery of TOI concentrations where thiosulfate showed the least TOI recovery. Ascorbic acid has been recently recommended by many studies as suitable quenching agent for preserving organic DBPs including THMs, HAAs and many others (Kristiana et al. 2014). However, this contradicts our results, where all TOX species except for TOI exhibited lower recoveries than other quenching agents. In these studies, DBPs have been

monitored using GC-MS instrument not by TOX, therefore, it's expected that ascorbic acid may interfere with TOX analysis method not necessary by inducing degradation of TOX during preservation. Ascorbic acid may compete with TOX organic compounds on AC sites during adsorption, thus reducing total TOX recovery. However, ascorbic acid was the most suitable for TOI and this agreed with a recent study that recommended using ascorbic acid as quenching agent for polar iodinated DBPs (Gong et al. 2016). Therefore, more research is needed to investigate ascorbic acid reactions with TOI during preservation. The results also in Fig 2.3 demonstrated that all TOX quenched samples were degraded by < 10% at 72 h holding time regardless of quenching agent and concentration used.

Therefore, to ensure TOX is stable in the presence of quenching agents at 4 °C and pH 7, the following steps should be considered; 1) sodium sulfite is recommended be used as quenching agent for, TOCl (Cl_2) and TOCl (NH_2Cl), where sodium thiosulfate for TOBr and ascorbic acid for TOI. 2) Overdosing of quenching agents must be avoided and 200 µM is maximum recommended dose for the quenching agents examined in this experiment. 3) Samples should not be stored for more than 72 h to avoid sever TOX degradation in the presence of quenching agents.

2.3.4 Impact of Acidification on TOX Stability

Fig 2.4 presents the impact of dropping pH to 2 using nitric, sulfuric and phosphoric acid on the stability of the four TOX species after 14 days at 4 °C. Results showed that dropping pH to 2 enhanced the recovery of TOX species in contrast to the TOX samples preserved at neutral pH. Recoveries for TOCl (Cl_2), TOBr, TOI and TOCl (NH_2Cl) were 91.9, 90.6, 86.9 and 83.7% when persevered at pH 7, 4 C and for 14 days.

However, when pH dropped to 2 using nitric acid, recoveries increased to averaged 94.2% for all four TOX species. Therefore, it essential to drop pH to 2 when storing TOX samples for any period of time at low temperatures to maintain stable TOX. Using sulfuric or phosphoric acid to lower the pH also resulted similar increase in TOX recoveries for TOCl (Cl_2), TOBr, and TOCl (NH_2Cl). However, when used for TOI, they resulted in substantial increase in TOI averaged 280 and 258% for sulfuric or phosphoric acid, respectively. Therefore, these acids caused a severe unidentified contamination for TOI analysis and must be avoided when treating TOI samples at low pHs.

Since acidifying TOX samples using nitric acid can maintain stable TOX concentrations during low temperature storage, it's important to investigate the impact of combining acidic pH and quenching agents on TOX recoveries during preservation. Sodium sulfite, sodium thiosulfate and ascorbic acid were added to TOX samples at 200 µM and at pH 2 using nitric acid. Afterwards, samples were stored at 4 °C refrigerate for 14 days before TOX analysis. Results shown in Fig 2.5 indicated that combining acidic pH and quenching agents (regardless of type) increased TOX recoveries substantially (> 80%) for all four TOX species. TOCl (Cl_2) and TOCl (NH_2Cl) samples dosed with sodium sulfite at pH 2 reported the most TOX recovery with 93.5 and 91.5%, respectively in contrast to the other quenching agents at pH 2. However, for TOBr, the combination of pH 2 and sodium thiosulfate resulted in 91.8% TOX recovery. Where for TOI, the most suitable combination was ascorbic acid at pH 2 with TOX recovery of 90.2% at the end of holding period. These results indicated that acidic pH can enhance TOX stability significantly in the presence of quenching agents during 14 days of storage at low temperatures. Therefore, TOX samples must be acidified to pH 2 using nitric acid

with/without quenching agents to maintain stable TOX (> 90%) for at least 14 days at 4 °C incubator.

2.3.5 Investigation on The Impact of Sulfuric and Phosphoric Acid on TOI Unexpected Formation

Fig 2.4 presented that when sulfuric or phosphoric acid is used to acidify TOI samples, unexpected TOI recovery was noticed. To identify this unexpected result, set of experiments have been conducted to evaluate the reaction of sulfuric acid with iodinated species. The hypothesis includes two parts 1) during holding period, sulfuric acid may react with the available iodinated organics and/or inorganic species in the presence of natural organic matter leading to TOX increase that interfere with TOI analysis. 2) sulfuric acid may interfere with TOI adsorption on activated carbon surface. To test the hypothesis, two sets of experiments have been conducted, the first monitored TOI formation over the storage period at 4 C (1-336 hr) in the presence of sulfuric acid. The second experiment investigated iodide adsorption on AC in the presence of sulfuric acid.

Fig 2.5 presents the impact of sulfuric acid on TOI ratios over 14 days of holding time at 4 °C. Results showed that the observed TOI unexpected formation was instantaneous starting from the first hour of incubation and then stabilized for the next 336 hrs. Therefore, this indicate that the TOX interference is not necessary caused by reactions of sulfuric species with TOI and may however resulted during TOI adsorption on AC on the presence of sulfuric acid. To test this idea, three samples have been prepared containing 1 mg/L of iodide at pH 7, pH 2 by nitric acid and pH 2 by sulfuric acid to investigate if iodide can be absorbed on AC. Samples went through AC adsorption immediately and rinsed with 15 mL of nitrate wash solution (1000 mg/L

NO_3^-), then subjected to TOX analysis. The specific 1 mg/L of iodide concentration was used to simulate the actual inorganic iodide present in TOI samples since 1 mg/L of I_2 was used to produce TOI. Results showed that iodide at pH 7 and pH 2 by nitric acid was totally flushed and no TOX was observed. However, TOX was detected in the sulfuric acid sample at 230% recovery, similar to what has been observed with acidic TOI samples with 280% recovery. This leads to the conclusion that sulfuric acid can alter AC surface to absorb iodide that cannot be rinsed by nitrate wash and thus causing interference during TOI analysis. The same experiment has been repeated using phosphoric acid and led to the same conclusion. Therefore, sulfuric and phosphoric acid must be avoided during TOI analysis and only nitric acid can be utilized for accurate TOI measurement. Furthermore, in Fig 2.5 the impact of the combination of sulfuric acid and 200 µM sodium sulfite on TOI stability was also investigated. The results demonstrated that the presence of sulfite have reduced the interference of iodide on TOI analysis, where at 6 hr of incubation, TOI recovery was reduced to 176% and continue to drop until 67.3% at the end of the 14 days. This indicate that the presence of sulfite may help rinsing iodide ions during AC nitrate wash step and the reaction continue to enhance overtime. However, these results do not indicate that iodide was completely flushed, and TOI was the only available species at the end of incubation period. Regardless, nitric acid should be the only agent to be used for TOI examination.

2.4 Conclusions

This study investigated the impact sample temperature and nitrate rinse volumes on TOCl (Cl_2), TOBr, TOI and TOCl (NH_2Cl) stability during AC adsorption. Results demonstrated that the lower the sample temperature the higher TOX recoveries on the AC. On the contrast, the higher nitrate wash volume, the lower TOX recovered due to TOX flushing. Consequently, to enhance TOX recovery as much as possible, TOX samples should be introduced to the AC adsorption process at 4 °C and rinsed with 15 mL of nitrate solution (1000 mg/L NO_3^-). Furthermore, the study examined the stability of TOX species at the presence of quenching agents including sodium sulfite, sodium thiosulfate and ascorbic acid at 4 °C and pH 7. The results showed that no universal quenching agent was found for TOX spices. However, to reduce their impact, overdosing must be avoided (> 200 µM), since severe TOX degradation was observed at high concentrations of quenching agents. Moreover, TOX samples should not be stored for more than 72 h of holding time in the presence of quenching agent at pH 7 and 4 °C. Acidifying TOX samples to pH 2 in the presence of quenching agents is the best step to reserve TOX for 14 days of incubation at 4 °C using nitric, phosphoric or sulfuric acid. However, sulfuric and phosphoric acids must be avoided for TOI analysis since it causes unnecessary interferences.

Table 2.1: DBPs recovery under different storage temperatures

DBPs (C/C_0)	4 °C	10 °C	20 °C
TCAA	103 ± 2	99 ± 1	101 ± 2
DCAA	99 ± 1	98 ± 2	99 ± 1
MCAA	98 ± 2	98 ± 2	98 ± 2
TBAA	99 ± 2	97± 1	99 ± 3
DBAA	102 ± 2	97 ± 2	97 ± 2
MBAA	98 ± 2	98 ± 3	100 ± 2
TIAA	97 ± 1	101 ± 1	99 ± 1
DIAA	99 ± 1	100 ± 2	99 ± 1
MIAA	98 ± 2	99 ± 1	100 ± 2
Chloroform	98 ± 2	100 ± 2	99 ± 2
Bromofrom	102 ± 1	98 ± 1	100 ± 2
Iodoform	99 ± 1	100 ± 2	101 ± 1
DCAN	98 ± 1	98 ± 2	97 ± 2
DBAN	97 ± 2	100 ± 1	98 ± 1
DCAcAm	102 ± 1	98 ± 3	100 ± 1
CH	99 ± 3	98 ± 2	96 ± 2
TCNM	101 ± 2	99 ± 3	97 ± 2

a. Each C/C_0 shows the average and standard deviation from the duplication experiments.
b. Storage conditions = 6 h holding time at pH 2 by nitric acid

Table 2.2: TOX concentrations after different nitrate wash volumes

TOX (µg/L)	10 mL	15 mL	20 mL	30 mL	50 mL
TOCl (Cl_2)	537.2 ± 2	535.1 ± 1	529.7 ± 2	485.7 ± 2	462.8 ± 2
TOCl (NH_2Cl)	103.2 ± 1	102 ± 2	97.6 ± 1	85.3 ± 1	71.2 ± 1
TOBr	472.2 ± 2	470 ± 2	462.8 ± 2	428.6 ± 1	405.4 ± 1
TOI	335.2 ± 2	334 ± 1	325.7 ± 3	290.2 ± 1	272.4 ± 1

a. Each concentration shows the average and standard deviation from the duplication experiments.
b. potassium nitrate stock used = 1000 mg/L as nitrate

Table 2.3: Recovery of TOX in the presence of quenching agents

TOX	Dose (µM)	Ascrobic Acid	Sodium Thiosulfate	Sodium Sulfite
TOCl (Cl_2)	0		93.4 ± 0.2	
	40	89.3 ± 0.2	90 ± 0.1	90.6 ± 0.3
	200	86.8 ± 0.3	88.2 ± 0.2	89.1 ± 0.2
	1000	81.5 ± 0.2	82.8 ± 0.2	84.3 ± 0.2
TOBr	0		91.6 ± 0.1	
	40	83 ± 0.5	90.6 ± 0.6	85.6 ± 0.5
	200	81.2 ± 0.6	84.9 ± 0.6	84.5 ± 0.7
	1000	66.8 ± 0.7	76.5 ± 0.4	69.5 ± 0.5
TOCl (NH_2Cl)	0		83.5 ± 0.2	
	40	70 ± 0.5	74.1 ± 0.6	80 ± 0.7
	200	67.9 ± 0.6	71.8 ± 0.5	75 ± 0.6
	1000	32.2 ± 0.4	50.1 ± 0.5	57.7 ± 0.6
TOI	0		86.3 ± 0.3	
	40	74.8 ± 0.3	68.3 ± 0.7	70.4 ± 0.9
	200	65.6 ± 0.5	48.2 ± 0.7	56.8 ± 0.7
	1000	39.1 ± 0.8	20.1 ± 0.8	30.4 ± 0.7

a. Each recovery shows the average and standard deviation from the duplication experiments.
b. Storage conditions = 336 h (14 days) quenching time.

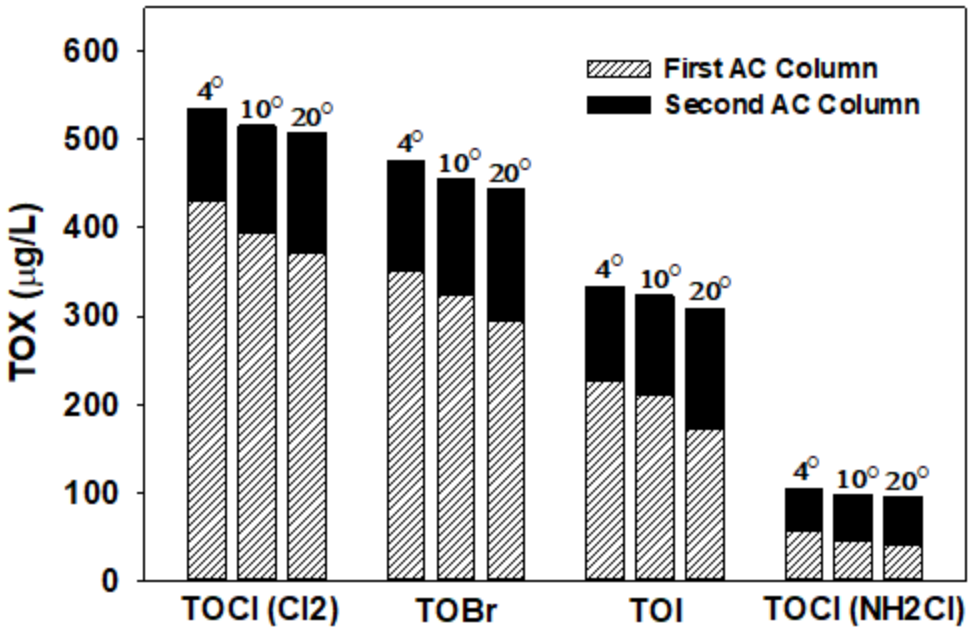

Figure 2.1: Total TOX concentrations and distribution under different sample storage temperatures

(6 hr storage before adsorption, pH 2 by nitric acid and 15 mL of nitrate wash using 1000 mg/L NO_3^- stock, TOX expressed as Cl_2, Br_2 and I_2)

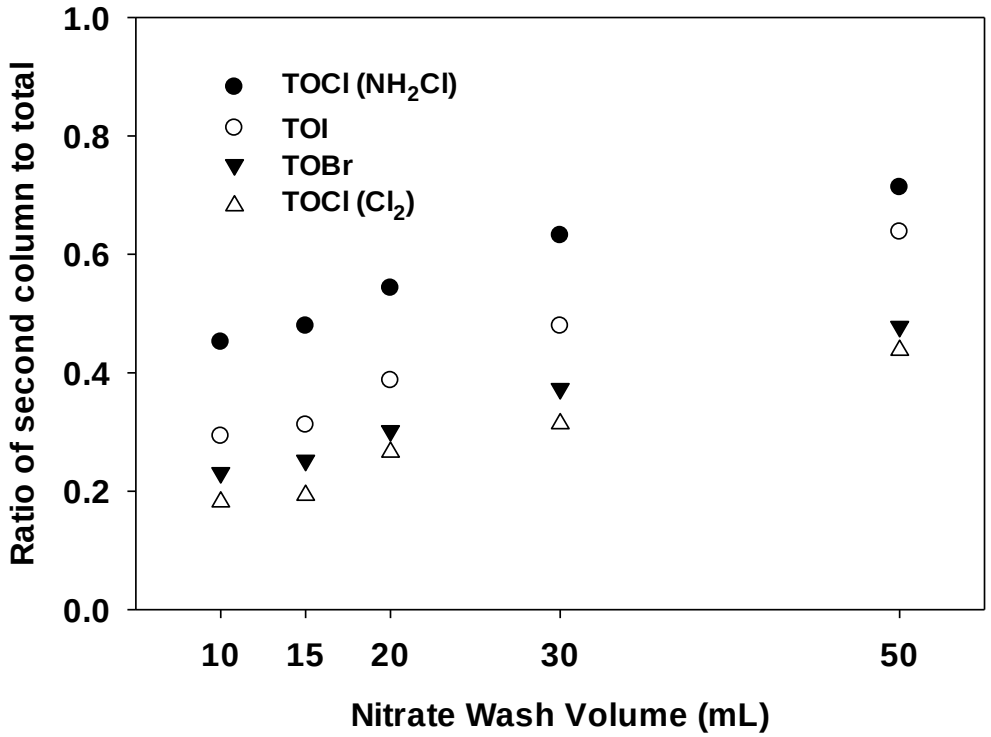

Figure 2.2: TOX recovery at the second AC column under different nitrate rinsing volumes

(6 h storage before adsorption at 4 °C, pH 2 by nitric acid and nitrate washing stock = 1000 mg/L NO_3^- stock).

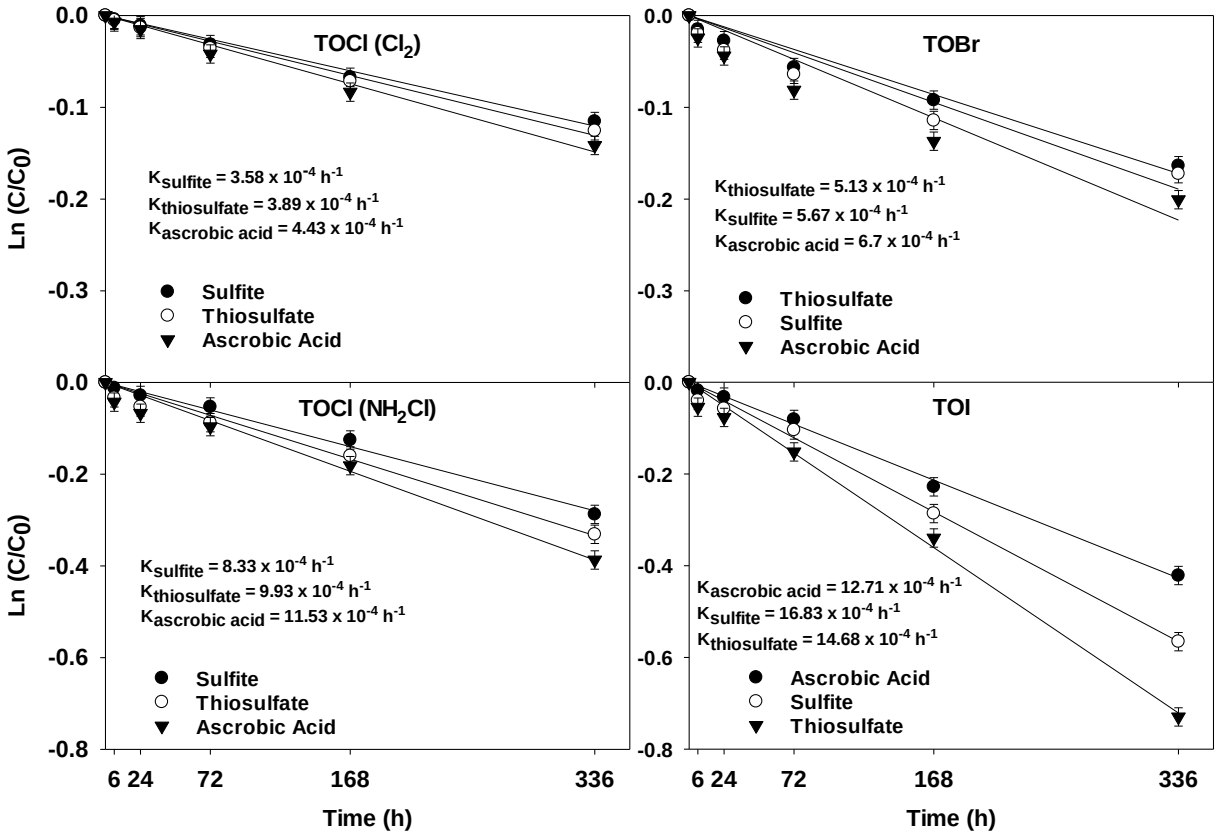

Figure 2.3: TOX degradation kinetics in the presence of quenching agents

(quenching agent concentration = 200 µM, sample storage at 4 °C, pH 7 dropped to 2 by nitric acid immediately prior to AC adsorption, and 15 mL of nitrate wash volume using 1000 mg/L NO_3^- stock, Error bars indicate standard deviations obtained from duplicate experiments. k=first order rate constant; $t_{1/2}$=half-life.)

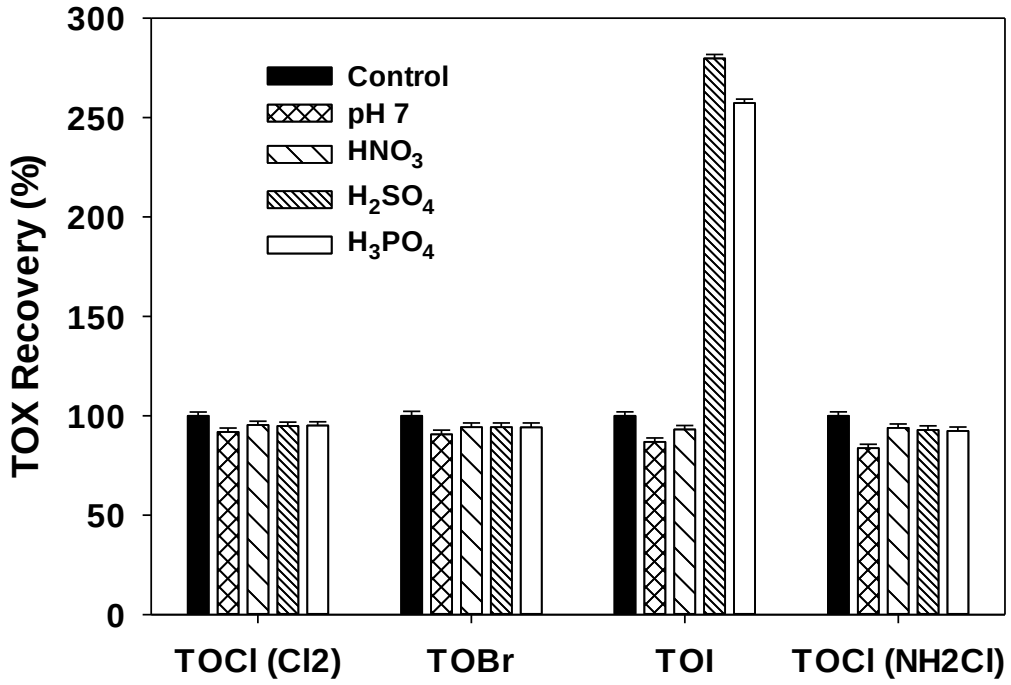

Figure 2.4: TOX recovery at acidic pH using different acid agents

(336 h storage at 4 °C, pH 2 and 15 mL of nitrate wash volume using 1000 mg/L NO_3^- stock, Error bars indicate standard deviations obtained from duplicate experiments.)

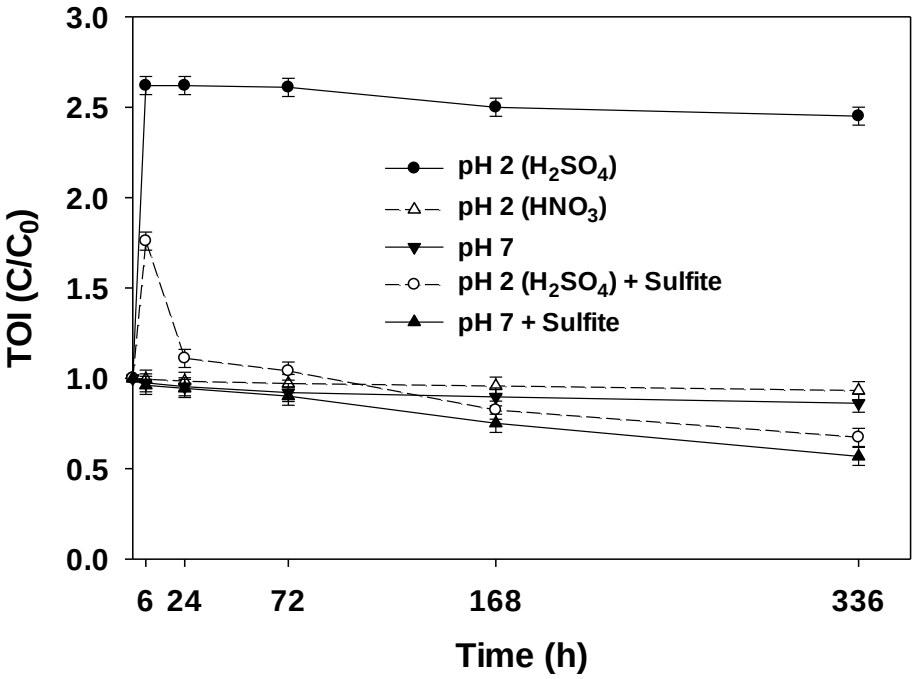

Figure 2.5: TOI formation during preservation by sulfuric acid

(quenching agent concentration = 200 µM, samples stored at 4 °C and washed with 15 mL of nitrate using 1000 mg/L NO_3^- stock, Error bars indicate standard deviations obtained from duplicate experiments.)

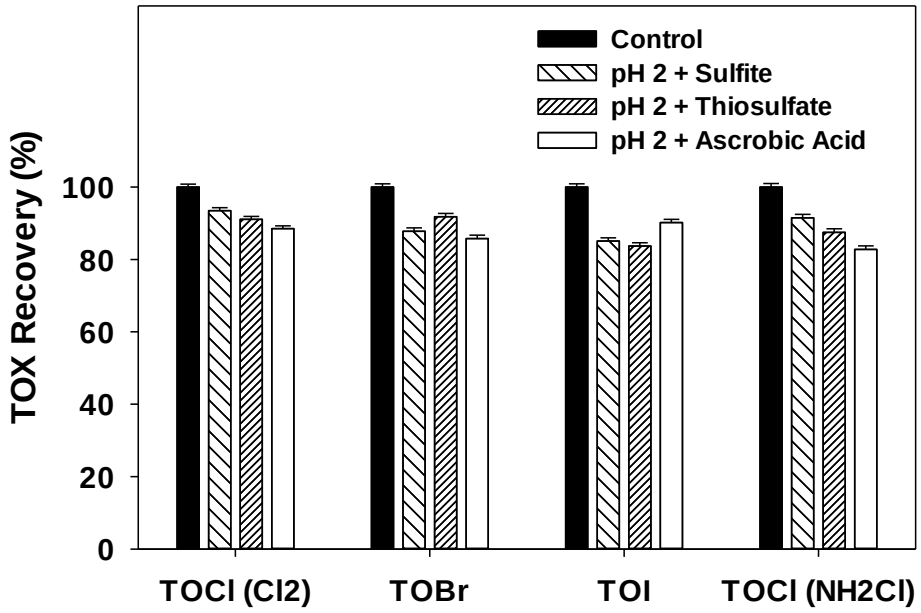

Figure 2.6: TOX recovery under the combination of acidic pH and quenching agents

(quenching agent concentration = 200 µM, pH 2 by nitric acid, samples stored at 4 °C for 336 h and washed with 15 mL of nitrate using 1000 mg/L NO_3^- stock, Error bars indicate standard deviations obtained from duplicate experiments).

CHAPTER THREE
NATURAL SOLAR PHOTOLYSIS OF TOTAL ORGANIC CHLORINE, BROMINE AND IODINE IN WATER

Abstract

Municipal wastewater has been increasingly used to augment drinking water supplies due to the growing water scarcity. Wastewater-derived disinfection byproducts (DBPs) may negatively affect the aquatic ecosystems and human health of downstream communities during water reuse. The objective of this research was to determine the degradation kinetics of total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI) in water by natural sunlight irradiation. Outdoor solar photolysis experiments were performed to investigate photolytic degradation of the total organic halogen (TOX) formed by fulvic acid and real water and wastewater samples. The results showed that TOX degradation by sunlight irradiation followed the first-order kinetics with half-lives in the range of 2.6 to 10.7 h for different TOX compounds produced by fulvic acid. The TOX degradation rates were generally in the order of TOI > TOBr ≅ TOCl(NH_2Cl) > TOCl(Cl_2). High molecular weight TOX was more susceptible to solar photolysis than corresponding low molecular weight halogenated compounds. The nitrate and sulfite induced indirect TOX photolysis rates were less than 50% of the direct photolysis rates under the conditions of this study. Fulvic acid and turbidity in water reduced TOX photodegradation. These results contribute to a better understanding of the fate of chlorinated, brominated and iodinated DBPs in surface waters.

3.1 Introduction

Municipal wastewater has become an increasingly important source of water due to the growing scarcity of potable water supplies worldwide. Water reclamation, recycling and reuse programs have been rapidly developed to mitigate the shortage of drinking water supplies in recent years (Rodriguez et al., 2009). In addition to the planned reuse, unplanned or incidental use of treated wastewater has taken place for several decades. Although the benefits of using wastewater to augment drinking water supplies have been well recognized, water reuse practices have also drawn serious concerns about potential health risks associated with the contaminants in treated effluents (Snyder et al., 2003).

Chlorine disinfection is a common process used by wastewater treatment plants (WWTPs) to inactivate pathogenic microorganisms before the effluent discharge. During the disinfection process, chlorine can react with effluent organic matter and bromide and iodide ions to form a variety of disinfection byproducts (DBPs), including trihalomethanes (THMs), haloacetic acids (HAAs), chloral hydrate, haloacetonitriles, nitrosamines and others (Mitch and Sedlak, 2002; Yang et al., 2005; Krasner et al., 2009). Toxicological and epidemiological studies have linked carcinogenic and developmental effects to exposure to DBPs in drinking water (Richardson, 2007). The United States Environmental Protection Agency currently regulates four THMs and five HAAs in drinking water in an effort to reduce the health risks associated with DBPs. Therefore, wastewater-derived DBPs may negatively affect the aquatic ecosystems and human health of downstream communities during water reuse.

The fate and transport of wastewater-derived DBPs in aquatic environments can be affected by several major biogeochemical processes including sorption, hydrolysis, biodegradation, volatilization and photolysis (Plumlee and Reinhard, 2007; Chen et al., 2008; Jin et al., 2012). Hydrolysis, biodegradation and volatilization can selectively remove certain species of DBPs such as haloketones (hydrolysis), dihalogenated acetic acids (biodegradation), and trihalomethanes (volatilization). Previous studies on solar photolysis of DBPs have focused on the degradation kinetics of specific DBPs (Lifongo et al., 2004; Chen et al., 2010). Nitrosamines were found to be highly photodegradable and the half-lives were less than 16 minutes under sunlight irradiation (Plumlee and Reinhard, 2007; Chen et al., 2010). Chlorinated THMs and HAAs were generally resistant to solar photolysis. Brominated and iodinated DBPs were more photosensitive than their chlorinated analogues based on solar irradiation experiments and quantitative structure-activity relationship analysis (Chen et al., 2010).

It has been recognized that a large portion of the DBPs formed by chlorine and chloramines have not been chemically identified yet. THMs, HAAs and other specific DBPs collectively accounted for less than 50% of the total organic halogen (TOX) formed by chlorine. When chloramine was used, more than 80% of the TOX remained unknown (Zhang et al., 2000; Hua and Reckhow, 2008a). The unidentified DBPs may contain many toxicologically important compounds that contribute substantially to the observed adverse health effects associated with drinking water DBPs (Bull et al, 2001; Richardson et al., 2007). Little is known about the impact of sunlight on unidentified DBPs in surface waters. Moreover, brominated and iodinated DBPs are likely present in WWTP effluents at relatively high levels because of the contamination from industrial

wastewater, hospital wastewater and other anthropogenic activities (Krasner et al., 2009; Duirk et al., 2011; Parker et al., 2014). The bromine and iodine containing DBPs are more cytotoxic and genotoxic than their chlorinated analogues according to toxicity studies (Plewa and Wagner, 2009). The unregulated and unidentified DBPs derived from wastewater treatment may pose significant risks to public health during water reuse practices because these DBPs are typically not monitored by water utilities.

With the rapid development of water reuse programs, we need to acquire a better understanding about the fate and transport of wastewater-derived DBPs (especially unregulated and unidentified species) in surface waters. The primary objective of this research was to determine the degradation kinetics of total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI) under natural sunlight irradiation conditions. In this study, we used fulvic acid and real water and wastewater samples as precursors to produce TOX compounds for outdoor photolysis experiments. The impact of pH, dissolved organic matter, nitrate, sulfite, turbidity and molecular weight fractions on solar photolysis of TOX was evaluated. The results of this research provide information about the photolytic degradation kinetics of total halogenated organic DBPs by natural sunlight irradiation. This knowledge can help us better understand the fate of chlorinated, brominated and iodinated DBPs in surface waters and develop strategies to reduce the health risks associated with wastewater-derived DBPs during water reuse.

3.2 Experimental Methods

3.2.1 Preparation of TOX Samples

The samples used for TOX formation during this study included solutions of Suwannee River Fulvic Acid (SRFA), a wastewater sample collected from the filter

effluent of the Brookings WWTP, SD, and a drinking water sample collected from the filter effluent of the Brookings Water Treatment Plant (WTP), SD. All solutions used in this study were prepared with ultrapure water (18 MΩ-cm) produced by a Barnstead NANOpure system. The chemicals used in this study were of American Chemical Society reagent grade and were purchased from Fisher Scientific (Fairlawn, NJ) unless otherwise noted. The SRFA was obtained from the International Humic Substances Society and dissolved in water at a dissolved organic carbon (DOC) concentration of 3 mg C/L. The SRFA solutions were treated with chlorine (3 mg/L as Cl_2), monochloramine (0.4 mg/L as Cl_2), bromine (2 mg/L as Br_2) and iodine (1 mg/L as I_2), respectively, to produce TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI for subsequent solar photolysis experiments. The SRFA oxidation experiments were conducted with 300 mL chlorine-demand free glass bottles on samples buffered with 1 mM phosphate at pH 7. After being dosed with each oxidant, the SRFA samples were stored head-space free at 20 °C in the dark for 72 hours. These experimental conditions were chosen so that each oxidant was completely consumed and no residual was found at the end of 72-hour incubation time. No quenching chemicals were used in this study to avoid their potential impact on photodegradation of TOX. Relatively high bromine and iodine doses were used in this study to produce large amounts of TOBr and TOI for better quantification of the degradation kinetics by solar photolysis (Moran et al., 2002; Magazinovic et al., 2004; Hua and Reckhow, 2006). The resulting TOX concentrations before photolysis experiments were 464±21 μg Cl/L for TOCl(Cl_2), 47±2 μg Cl/L for TOCl(NH_2Cl), 278±10 μg Br/L for TOBr and 144±6 μg I/L for TOI, respectively, for a total of five sets of experiments. The experimental conditions for TOX formation from fulvic acids were

kept the same during this study to produce similar TOX compounds for evaluating the impact of different factors on TOX photolysis. It should be noted that variations in the oxidation conditions (e.g., dose, pH, reaction time, temperature and others) would affect the TOX concentrations and properties, which may subsequently impact the natural photolysis of these compounds. It is recommended that further studies be done on TOX compounds produced by different treatment conditions.

The stock solutions of chlorine, bromine and iodine were prepared by diluting a sodium hypochlorite solution (4-6%, Fisher Scientific) and a bromine solution (>99.5%, Sigma Aldrich, St Luis, MO), and by dissolving solid iodine (>99.8%, Sigma Aldrich) in water, respectively. The stock monochoramine solution was created by mixing aqueous ammonium sulfate and sodium hypochlorite solutions at a Cl_2/N molar ratio of 0.8:1. The pH of both solutions was adjusted to 8.5 using sulfuric acid or sodium hydroxide before mixing. The halogen stock solutions were standardized by the DPD ferrous titrimetric method (APHA et al., 2012).

Chlorination and chloramination were performed for the wastewater and drinking water samples to produce TOX solutions for solar photolysis experiments. The chlorine and chloramine doses were 8 mg/L and 0.8 mg/L, respectively, for Brookings wastewater sample, and 2.5 mg/L and 0.35 mg/L, respectively, for Brookings drinking water sample. These doses were determined through preliminary demand tests such that all chlorine and chloramine were completely consumed and no residual was found at the end of 72-hour incubation time. Other experimental conditions were kept the same as the SRFA oxidation experiments.

3.2.2 Natural Solar Photolysis Experiments

Natural solar photolysis experiments were performed using 60 mL quartz tubes with an outside diameter of 25 mm and a length of 150 mm. The thickness of the tube wall is 1.5 mm. The quartz tubes were capped to prevent the volatilization and evaporation of TOX samples during the photolysis experiments. The sample tubes were placed on fabricated platforms at a 30^{o} angle. The outdoor solar photolysis experiments were conducted between May and September 2014, in an open space adjacent to the Water and Environmental Engineering Research Center in Brookings, SD, USA (44°18'53.5"N, 96°47'09.7"W). Each set of photolysis experiments was started at 11:30 am on the testing day and extended for a total of 6 hours of sunlight exposure. The solar radiation intensity (W/m^2) was recorded on-site every 30 minutes using a photometer (Seaward 396A916, Tampa, FL). The average solar radiation intensities varied between 1052 and 1140 W/m^2 and the average temperatures varied between 25 and 28 ^{o}C during a total of 6 sets of photolysis experiments. The cloud cover was also monitored throughout the experiments, and the duration of each photolysis experiment was extended, if necessary, to achieve the target 6 hour solar exposure. Detailed information about the variation of solar intensities, temperatures and cloud conditions for the photolysis experiments is reported in Table 3.1 and Figure 3.1.

A total of five sets of outdoor photolysis experiments were performed to evaluate the impact of pH, molecular weight (MW), nitrate, sulfite, and fulvic acid on photodegradation of the TOX produced by SRFA. First, each treated SRFA sample was subject to solar irradiation for 0, 0.5, 1, 2, 4, and 6 hours at three different pH conditions (6, 7, and 8). Sulfuric acid or sodium hydroxide solutions were added to photolysis tubes

to adjust the sample pHs to 6 and 8, respectively, before the experiment. No adjustment was needed for the pH 7 samples. Second, each treated SRFA sample was separated by a Millipore PLAC ultrafiltration membrane (EMD Millipore, Billerica, MA) with MW cutoff of 1 kDa into low MW (<1kDa) and high MW (>1kDa) TOX fractions. Ultrafiltration was performed with a stirred 350 mL Amicon ultrafiltration cell. For an initial sample volume of 350 mL, the filtration was stopped when the volume of retentate decreased to 75 mL. Permeate was collected and this fraction was referred to as low MW fraction. Organic-free deionized water was added to the cell to bring the volume back to 350 mL and filtration was continued until the volume decreased to 75 mL again. This process was repeated three times to remove compounds with MW lower than the membrane cut-off. Then, the retentate (high MW fraction) was collected and the volume was diluted to 350 mL with deionized water. The TOX fractions were subject to solar irradiation for 0 to 6 hours at pH 7. During the last three sets of SRFA TOX photolysis experiments, each sample was spiked with different levels of nitrate (0-20 mg/L), sulfite (0-5 mg/L), or SRFA (0-20 mg/L) separately to investigate the impact of these water quality parameters on TOX photodegradation. Potassium nitrate, sodium sulfite, and SRFA solutions were added to sample tubes to achieve the target levels. After being dosed with each of these chemicals, the TOX samples were subject to solar irradiation for 0 to 6 hours at pH 7.

The wastewater and drinking water TOX samples were also exposed to natural sunlight irradiation for 0 to 6 hours at pH 7. In addition, a river water sample was collected and mixed with the wastewater and drinking water samples to evaluate the impact of natural water matrix on TOX photolysis. The river water sample was taken

from the Big Sioux River near Brookings, SD. The Big Sioux River watershed is characterized by its rural environment with limited industrial development, and is highly impacted by agricultural activities. The treated wastewater and drinking water samples were mixed with the raw river water samples or filtered river samples (by 0.45 μm membranes) separately at a ratio of 1:1. The mixtures were then subject to solar irradiation for 0 to 6 hours at pH 7.

All solar irradiation experiments were conducted in duplicate. Dark control experiments were also performed simultaneously for each set of samples. The dark control sample tubes were wrapped with aluminum foil, and placed in a box adjacent to the solar photolysis platforms. The control samples were taken at different time intervals (0-6 hours) to determine the possible TOX degradation kinetics in the dark.

3.2.3 Analytical Methods

Chlorine, chloramine, bromine and iodine residuals were analyzed by the DPD ferrous titrimetric method (APHA et al., 2012). The DOC concentrations were determined with a Shimadzu TOC-5000 Analyzer (Shimadzu Corp., Kyoto, Japan) according to Standard Method 5310 B (APHA et al., 2012). A DX-500 ion chromatography system (Dionex, Sunnyvale, CA) equipped with a conductivity detector (CD-20, Dionex) was employed to measure bromide, iodide and nitrate ion concentrations. The TOX samples were acidified to pH 2 by concentrated nitric acid immediately after sampling and stored at 4 °C before the analysis. The TOX was determined by an adsorption-pyrolysis-titration method with a Mitsubishi TOX-100 Analyzer (Cosa Xentaur Inc., Norwood, NJ). The method was based on standard method 5320 B with minor modifications (APHA et al., 2012). TOX recovery tests were

performed on specific DBPs including bromoform, iodoform, dichloroacetonitrile, monoiodoacetic acid, dichloroacetic acid, dibromoacetic acid, and trichloroacetic acid. The recoveries of these DBPs by the TOX method were between 95 and 105%, which are very similar to a previous study (Hua and Reckhow, 2006). Because pure chlorine, chloramine, bromine and iodine solutions were used for SFRA samples and no bromide and iodide was found in SRFA solutions, the TOX results from the SRFA experiments were expressed as halogen-specific TOX concentrations.

3.3 Results and discussion

3.3.1 Degradation Kinetics of TOCl, TOBr and TOI by Solar Photolysis

Figure 3.2 shows the impact of pH and time on the degradation of TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI under natural solar photolysis conditions. The TOX stability in the dark was evaluated through the dark control experiments. The TOX reduction for each sample was less than 4% after 6 hour incubation in the absence of sunlight irradiation (Table 3.2), suggesting that the dehalogenation of these TOX compounds at pH 6-8 in the dark was insignificant under the conditions of this study. Each group of TOX compounds exhibited appreciable photolytic dehalogenation within 6 hours of solar irradiation. The average reductions in TOX at pH 7 were 38%, 46%, 50%, and 67% for TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI, respectively, after 6 hours of sunlight exposure. This result suggests that carbon-halogen bonds in the TOX compounds could be photo-cleaved by natural sunlight irradiation and, iodinated and brominated DBPs were more susceptible to photodegradation than chlorinated DBPs. The higher dehalogenation rates of TOI and TOBr than TOCl(Cl_2) could be attributed in part to the difference in the carbon-halogen bond dissociation energies: 397, 280, 209 kJ/mol for C-Cl, C-Br, and C-I bonds, respectively (Weast et al., 1986). Higher bond dissociation

energy indicates a higher resistance to deformation during chemical reactions. The results of these TOX solar photolysis experiments qualitatively agree with previous photolysis studies using specific DBPs that showed iodine- and bromine-substituted species were more photosentitive than chlorinated analogues (Lekkas and Nikolaou 2004; Chen et al., 2010; Fang et al., 2013; Jo et al., 2011; Xiao et al., 2014). Chloramination TOX also exhibited a higher dehalogenation degree than chlorination TOX suggesting that chloraminated DBPs were relatively less stable and more photosensitive than chlorinated DBPs under sunlight irradiation. This may be related to the differences in physical and chemical properties of these two groups of DBPs. For example, it has been shown that TOX formed by chloramine and humic substances contained higher percentages of high MW compounds than chlorination TOX (Hua and Reckhow, 2008b). The low monochloramine dose (0.4 mg/L) used in this study might also affect the physical and chemical properties of chloramine TOCl (Hua and Reckhow, 2008b).

The results in Figure 3.2 also showed that the pH value had substantial impact on photolysis of the TOX compounds. The dehalogenation degrees of each TOX group increased with increasing pH values. For a solar exposure of 6 hours, the TOX degradation degrees increased by 11, 17, 19, and 28 percentage points for TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI, respectively, when increasing the photolysis pH from 6 to 8. It is clear from these results that photodegradation of halogenated DBPs by sunlight irradiation was enhanced under alkaline conditions. Few studies have evaluated the impact of pH on photolysis of DBPs. Wu et al. (2001) reported little influence of pH on the degradation rate of trichloroacetic acid by UV light in the pH range of 1.1-11.2. However, Fang et al. (2013) showed that photolysis kinetics of bromo-, dibromo-, and

dichloronitromethanes increased by 14 to 98 times when increasing pH from 4 to 9. It was thought that these weak acids (pKa 6.0-7.6) halonitromethanes dissociated into deprotonated forms accompanied by the formation of conjugation systems at basic pHs, which strongly increased the UV absorption and facilitated the photodegradation of these compounds. It is expected that typical pH values in natural waters would have limited influence on the solar photolysis of regulated THMs (pKa>11) and HAAs (pKa<3) due to their acid-base dissociation constants. The observed pH impact on the solar photolysis of the TOX compounds formed by fulvic acid may be attributed to unregulated and unidentified DBPs that have acid-base dissociation constants (pKa) close to the pH range tested in this study. It can be inferred that the deprotonated forms of TOX compounds at high pH values may be more photosensitive than the protonated forms under natural sunlight irradiation.

Table 3.3 summarizes the pseudo-first-order rate constants (kp), calculated half-lives, and linear regression coefficients (R^2) for solar photolysis of the four TOX groups. The photolytic degradation of TOX compounds followed the first-order kinetics as evidenced by the relatively high R^2 values (> 0.98). The half-lives were 7.2-10.7 h, 5.1-8.6 h, 4.6-7.8 h, and 2.6-6.0 h for TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI, respectively, under natural sunlight irradiation at pH 6-8. The first-order rate constants increased by 49% (TOCl(Cl_2)) to 133% (TOI) when increasing pH to 8 from 6. This confirms that high pH conditions enhanced the degradation of these TOX compounds by sunlight irradiation. Chen et al. (2010) evaluated the photolytic degradation of chlorinated and brominated THMs and HAAs by natural sunlight. The experimental results were used to predict the photolysis potentials of iodinated DBPs through quantitative structure-activity

relationship analysis. Their results showed that the predicted rate constants were related to the number of halogens (tri-> di-> mono-halogenated) and the size of the halogen substituted (I>Br>Cl). The determined half-lives were 11.2 h, 2.0 h, and 8 min for chloroform, bromoform, and iodoform, respectively. Chlorinated and brominated HAAs were relatively stable in water with half-lives between 18 h (tribromoacetic acid) and 2889 h (trichloroacetic acid). However, relatively fast decay rates were expected for mono- (3.4 h), di- (6.3 min) and triiodoacetic acids (11 s).

The TOX photodegradation results in this study also showed that iodinated and brominated DBPs degraded faster than chlorinated DBPs under sunlight irradiation. However, the differences in the rate constants of TOCl, TOBr, and TOI were much less pronounced than that of specific DBPs with different substituted halogens. For example, the predicted photolytic degradation rate constants of iodoform and triiodoacetic acid were two and five orders of magnitude higher than chloroform and trichloroacetic acid. This indicates that some of the TOI compounds formed by fulvic acid may be more persistent than specific I-DBPs under natural sunlight irradiation. Certainly, further studies are needed to verify the predicted rate constants for specific I-DBPs. In general, the solar photolytic degradation rates of the four groups of TOX compounds were in the order of TOI > TOBr ≅ TOCl(NH_2Cl) > TOCl(Cl_2).

3.3.2 Degradation Kinetics of High and Low MW TOX by Solar Photolysis

Ultrafiltration with 1kDa membranes was used to isolate the TOX compounds formed by fulvic acid into high and low MW groups (Figure 3.3). The percentages of the TOX fractions with MW higher than 1kDa were 47%, 72%, 74%, and 79% for TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI, respectively. This demonstrates that the TOX

formed by fulvic acid and chloramines, bromine, and iodine consisted mainly of high MW compounds. Hua and Reckhow (2008b) also reported that chloramination of humic acid resulted in higher percentages of high MW TOX than chlorination. Both studies suggest that free chlorine is able to fragment NOM molecules and shift the TOX compounds toward to smaller sizes whereas a large amount of chloramination TOX may be formed by halogen substitution into organic molecules without extensive structural modification. Bromine and iodine also produced relatively high percentages of high MW (>1 KDa) TOX compounds from the reactions with fulvic acid. Similar to chloramination, the halogenated DBPs formed by bromine and iodine were predominantly high MW compounds that could not be accounted for by known specific DBPs such as THMs and HAAs.

Figure 3.4 presents the first-order photolysis kinetics of high and low MW TOX fractions. For each TOX group, the high MW (>1 KDa) TOX fraction degraded faster than the corresponding low MW (< 1KDa) fraction. This indicates that high MW DBPs were more photosensitive than low MW DBPs and the high MW TOX compounds were more effectively cleaved by photochemical reactions under sunlight irradiation. It can be inferred from Figure 3.4 that the unknown and unidentified DBPs (predominantly high MW compounds) are perhaps less stable than known specific DBPs (THMs and HAAs) in surface waters under natural sunlight irradiation. Although a general trend was observed regarding the impact of MW on TOX photolysis, the four groups of TOX compounds exhibited distinct differences in relative variations in rate constants of the two fractions. The TOCl(Cl_2) compounds showed the largest difference (132%) in the rate constants of the two MW fractions whereas the TOI compounds exhibited the smallest

difference (23%). The rate constants variations of the two fractions of TOCl(NH_2Cl) and TOBr were 67% and 83%, respectively. These observations suggest that chlorine-substituted DBPs with high MW were much more photosensitive than the corresponding low MW fraction whereas iodinated DBPs exhibited relatively high photolysis degrees for both high and low MW fractions.

3.3.3 Effect of Nitrate, Sulfite and Fulvic Acid on TOX Degradation by Solar Photolysis

Indirect photolysis has been recognized as an important photochemical process that degrades micropollutants in waters. NOM and nitrate are common photosensitizers in natural waters which can absorb the sunlight and transfer the energy to the pollutants. Sunlight excitation of nitrate ions in water results in the formation of $^{\bullet}OH$ radical and various nitrogen reactive species ($NO^{\bullet}$, $NO_2^{\bullet}$, etc.) that can react with many organic and inorganic contaminants (Keen et al., 2012). NOM present in water can have two opposite effects on solar photolysis process. Sunlight irradiation of NOM can lead to the formation of excited triplet sates of NOM (3NOM*) or singlet state of NOM (1NOM*). Subsequent reactions between 3NOM* and oxygen produce singlet molecular oxygen ($^1O_2$). These NOM induced reactive species can increase the photodegradation rates of pollutants (Bahnmuller et al., 2014; Janssen et al., 2014). NOM can also have inhibiting effect on photolysis reactions primarily due to the filtering effect of light by the organic molecules (Xiao et al., 2014). Sulfur-based reducing agents such as sulfur dioxide and sulfite are commonly used by WWTPs to remove chlorine residuals prior to discharge to surface waters. These reducing agents have been shown to degrade some of the halogenated DBPs (Croue and Reckhow, 1989). In addition, irradiation of sulfite ions in water with UV light generates sulfite anion radicals ($SO_3^{\bullet-}$) and aqueous electrons (e_{aq}^-) that can

degrade water contaminants (Li et al., 2012; Vellanki et al., 2013). The dissolved oxygen level was not controlled during the TOX solar photolysis experiment to simulate natural water conditions. In the presence of oxygen, sulfite radical reacts rapidly with O_2 to form a peroxyl radical ($SO_5^{\bullet-}$) which is a stronger oxidant that can oxidize many organic compounds (Neta and Huie, 1985). Figure 3.5 shows the impact of nitrate (0-20 mg/L) on solar photolysis of the TOX compounds. The first-order rate constant for nitrate induced photodegradation ($k_{nitrate*}$) was calculated based on the difference between the total photodegradation rate constant and the direct photolysis rate constant ($k_{sunlight}$) in the absence of nitrate. For each TOX group, the nitrate induced photodegradation rate increased with increasing nitrate concentrations. For an initial nitrate concentration of 5 mg/L, the indirect photolysis rate constants ($k_{nitrate*}$) were 0.003 h^{-1}, 0.022 h^{-1}, 0.018 h^{-1} and 0.047 h^{-1} for TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI, representing 3% (TOCl(Cl_2)) to 25% (TOI) of the direct photolysis rate constants ($k_{sunlight}$). When the nitrate concentration was increased to 20 mg/L, the indirect photolysis rate constants amounted to 14% (TOCl(Cl_2)) to 49% (TOI) of the direct photolysis rate constants. These results indicate that nitrate in water induced the degradation of halogenated DBPs through photosensitized reactions under natural sunlight irradiation. The TOI was more prone to the attack of nitrate induced radicals than other TOX compounds. However, the sunlight-nitrate indirect photolysis was generally insignificant compared to the direct photolysis at low nitrate concentrations (< 5 mg/L).

Nitrate photolysis has been identified as an important source of hydroxyl radicals in natural waters. Zepp et al. (1987) developed a model to estimate steady state $^{\bullet}OH$ radical concentrations ($[^{\bullet}OH]_{ss}$) for noon, midsummer conditions at the surface of water

bodies. The calculated $[^{\bullet}OH]_{ss}$ in Greifensee, Switzerland (1.4 mg/L of NO_3^--N and 4 mg/L of DOC) was 2.5×10^{-16} M. Brezonik and Fulkerson-Brekken (1998) calculated the $[^{\bullet}OH]_{ss}$ concentrations at the surface of several natural waters (0.13 – 8.8 mg/L of NO_3^--N and 2.36 – 7.45 mg/L of DOC) for midday and June conditions. The calculated $[^{\bullet}OH]_{ss}$ concentrations varied between 1.0×10^{-15} and 3.1×10^{-17} M. Similar ranges of $[^{\bullet}OH]_{ss}$ are expected under the conditions of this study (2-20 mg/L of NO_3^--N and 3 mg/L DOC). More studies are needed to determine the rates constants of nitrate-induced radicals and TOX compounds in order to predict the impact of nitrate on TOX photodegradation in natural waters. Based on the results of this study, the contribution of nitrate induced indirect photolysis to TOX degradation is expected to be much less than direct photolysis under typical natural water conditions.

Figure 3.6 presents the impact of sulfite (0-5 mg/L) on solar photolysis of the TOX compounds. It was found that sulfite itself was able to degrade TOX compounds in the dark and the TOX dehalogenation increased with increasing sulfite concentrations. For an initial sulfite concentration of 5 mg/L, the dehalogenation rate constants ($k_{sulfite}$) were 0.007 h^{-1}, 0.016 h^{-1}, 0.011 h^{-1} and 0.030 h^{-1} for TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI, representing 9% (TOCl(Cl_2)) to 15% (TOI) of the direct solar photolysis rate constants. Iodinated DBPs were less stable than brominated and chlorinated DBPs in the presence of sulfite. The sunlight-sulfite induced indirect photolysis rate constant ($k_{sulfite*}$) was determined based on the difference between the total photodegradation rate constant and the sum of direct photolysis rate constant ($k_{sunlight}$) and sulfite dehalogenation rate constant in the dark ($k_{sulfite}$) for each sulfite concentration. Similar to the sulfite dehalogenation rate constants, the sunlight-sulfite indirect photolysis rate constants

($k_{sulfite*}$) also increased with increasing sulfite concentrations, suggesting that the reactive species produced from sunlight-sulfite photosensitized reactions were able to degrade halogenated DBPs. The indirect photolysis rate constants ($k_{sulfite*}$) were very close to the sulfite dehalogenation rate constants ($k_{sulfite}$) when the sulfite concentration was less than 2 mg/L. Enhanced sunlight-sulfite indirect photolysis was observed when the sulfite concentration was increased to 5 mg/L. At this concentration, the rate constants ($k_{sulfite*}$) were 0.011 h^{-1}, 0.027 h^{-1}, 0.022 h^{-1} and 0.060 h^{-1} for TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI, representing 13% (TOCl(Cl_2)) to 31% (TOI) of the direct solar photolysis rate constants. Similar to nitrate, the contribution of sulfite induced indirect photolysis to TOX degradation is expected to be much less than direct photolysis for typical WWTP and natural water conditions.

Figure 3.7 presents the effect of fulvic acid on solar photolysis of the TOX compounds after 6 hours of sunlight exposure. Sunlight-NOM induced indirect phototransformation of halogenated DBPs was not observed for each TOX group. Instead, increasing fulvic acid concentrations inhibited the solar photolysis of halogenated DBPs. The reduction in TOX photodegradation extents was presumably caused by the screening effect of sunlight irradiation by fulvic acid. The light filtering effect on TOX photodegradation was more pronounced when the fulvic acid concentration was higher than 5 mg/L. Fulvic acid had limited impact on the photolysis extents of TOX when the concentration was less than 5 mg/L. The UV absorbance at 254 nm (UV254) of the TOX samples was used to quantify the light filtering effect of fulvic acid. The UV254 of each TOX solution before adding fulvic acid was 0.099, 0.115, 0.106 and 0.116 cm^{-1} for TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI, respectively. The

corresponding UV254 values increased to 0.947, 0.995, 0.981, and 1.004 cm^{-1} when increasing fulvic acid to 20 mg/L (Table 3.4). It is clear that the added fulvic acid substantially reduced the light transmittance, thereby inhibiting the solar photolysis of TOX compounds. The remaining TOX concentration after 6 hour sunlight exposure increased by 10, 25, 23, and 30% for TOCl(Cl_2), TOCl(NH_2Cl), TOBr and TOI, respectively, when increasing fulvic acid concentration from 0 to 20 mg/L. The reductions in TOX photodegradation extents by added fulvic acid were similar among TOCl(NH_2Cl), TOBr and TOI, whereas TOCl(Cl_2) exhibited the lowest reduction. This may be due to that TOCl(Cl_2) contains approximately 50% THMs and HAAs, which are generally resistant to solar photolysis.

3.3.4 Effect of Natural River Water Matrix on TOX Degradation by Solar Photolysis

Table 3.5 presents water quality characteristics of the filter effluents from Brookings water and wastewater treatment plants and a water sample collected from the Big Sioux River. The WWTP sample had a much higher DOC concentration than the WTP sample, which resulted in higher TOX formation during chlorination and chloramination. The bromide concentrations of the WTP and WWTP samples were relatively low. It was expected that chlorine substituted DBPs were the predominant species in the TOX compounds produced by chlorination and chloramination of the two samples. The Big Sioux River sample had medium levels of DOC, nitrate and turbidity.

Figure 3.8 shows the impact of the river water matrix on solar photolysis of the TOX compounds formed by the WTP and WWTP water samples. Sunlight irradiation resulted in dehalogenation of the TOX compounds in the treated water samples. The TOX reductions after 6 hour solar exposure were 35% (Cl_2) and 47% (NH_2Cl) for the

WWTP samples and 33% (Cl_2) and 46% (NH_2Cl) for the WTP samples. These photodegradation degrees were similar to the photolysis results of the TOX compounds formed by chlorination and chloramination of fulvic acid. Chloramination TOX showed higher dehalogenation extents than chlorination TOX for both samples, suggesting that chloraminated DBPs were more photosensitive than chlorinated DBPs. When the treated water samples were mixed with the filtered river sample, the mixtures had similar TOX photolysis extents to the treated water samples. This indicates that the dissolved water matrix (NOM, nitrate and others) in the river sample had little impact on the photolysis of halogenated DBPs after diluting with treated water samples. However, the unfiltered river sample substantially reduced the TOX photolysis extents of the treated water samples. The reductions were 23 and 22% for chlorinated and chloraminated WWTP samples and 12 and 26% for chlorinated and chloraminated WTP samples. The effects of the blended river water on the UV254 of treated water samples are presented in Table 3.6. After mixing with the unfiltered river water, the UV254 of the WWTP water samples increased by factors of 2 to 2.4, and the UV254 of the WTP water samples increased by factors of 20 to 25. It is clear that particles in the river sample reduced light penetration thereby inhibiting the photolytic degradation of halogenated DBPs. This result suggests that turbidity levels of surface waters can have a significant impact on the degradation of wastewater-derived DBPs by sunlight photolysis.

3.4 Conclusions

Treated municipal wastewater has been increasingly used to augment drinking water supplies to mitigate water shortage in many areas. The wastewater-derived DBPs can negatively affect the aquatic ecosystem and public health during water reuse. This study was conducted to investigate the photolytic degradation of total halogenated DBPs in water by natural sunlight irradiation. For the DBPs produced by fulvic acid, the TOX photodegradation under sunlight irradiation followed the first-order kinetics with half-lives in the range of 7.2-10.7 h for TOCl(Cl_2), 5.1-8.6 h for TOCl(NH_2Cl), 4.6-7.8 h for TOBr, and 2.6-6.0 h for TOI, respectively. In general, the TOX degradation rates were in the order of TOI > TOBr ≅ TOCl(NH_2Cl) > TOCl(Cl_2). The TOX degradation rate constants increased by factors of 1.5 to 2.3 when increasing pH from 6 to 8. High MW (> 1kDa) TOX fractions showed higher photodegradation rates than corresponding low MW (< 1KDa) TOX fractions.

Indirect photolysis of TOX was observed when nitrate and sulfite were present in water. The nitrate and sulfite induced indirect photolysis rates were less than 50% of the direct photolysis rates under the conditions of this study. Fulvic acid had little impact on the TOX photolysis rates when the concentration was less than 5 mg/L. However, TOX photodegradation was inhibited at higher fulvic acid concentrations. The solar photolysis experiments of wastewater and drinking water samples also showed that chloramination TOX was more photosensitive than chlorination TOX. The TOX photolysis rates were not substantially affected when the treated samples were mixed with a filtered river sample. However, the unfiltered river sample reduced the TOX photolysis extents by 12-26% for the treated water and wastewater samples.

Table 3.1: Weather conditions for TOX solar photolysis experiments

Testing Date	Photolysis Test	Temperature (^oC)	Average Solar Intensity (W/m^2)	Duration of Clouds (min)	Photolysis Time (CST)
5/29/2014	Impact of pH on TOX Photolysis	28 ± 1	1108	<10	11:30am – 5:30 pm
7/14/2014	Impact of Nitrate on TOX Photolysis	25 ± 1	1140	<10	11:30am – 5:30 pm
8/3/2014	TOX MW Fractions Photolysis	27 ± 2	1097	15	11:30am – 5:45 pm
8/14/2014	Impact of Sulfite on TOX Photolysis	27 ± 1	1087	30	11:30am – 6:00 pm
8/24/2014	Impact of Fulvic Acid on TOX Photolysis	27 ± 2	1052	15	11:30am – 5:45 pm
9/28/2014	Real Water Samples Photolysis	26 ± 3	1112	<10	11:30am – 5:30 pm

Table 3.2: TOX Variation after Six Hours in the Dark

C/C_0	$TOCl(Cl_2)$	$TOCl(NH_2Cl)$	TOBr	TOI
pH 6	99 ± 1 %	99 ± 2 %	99 ± 1 %	99 ± 2 %
pH 7	98 ± 1 %	99 ± 1 %	98 ± 1 %	98 ± 1 %
pH 8	98 ± 1 %	98 ± 2 %	98 ± 2 %	98 ± 2 %

Each C/C_0 shows the average and standard deviation from the duplication experiments.

Table 3.3: First order rate constants for solar photolytic dehalogenation of TOCl, TOBr, and TOI formed by fulvic acid

TOX	pH	k (h^{-1})	Half-life (h)	R^2
TOCl(Cl_2)	6	0.065 ± 0.001	10.7 ± 0.2	0.996
	7	0.081 ± 0.001	8.5 ± 0.1	0.999
	8	0.097 ± 0.003	7.2 ± 0.3	0.989
TOCl(NH_2Cl)	6	0.081 ± 0.002	8.6 ± 0.3	0.990
	7	0.106 ± 0.002	6.6 ± 0.2	0.995
	8	0.136 ± 0.003	5.1 ± 0.2	0.992
TOBr	6	0.090 ± 0.003	7.8 ± 0.3	0.989
	7	0.119 ± 0.003	5.9 ± 0.2	0.992
	8	0.151 ± 0.005	4.6 ± 0.2	0.984
TOI	6	0.115 ± 0.003	6.0 ± 0.2	0.992
	7	0.183 ± 0.007	3.8 ± 0.2	0.983
	8	0.268 ± 0.008	2.6 ± 0.1	0.989

a. Photolysis experiments date= 05/29/2014; average solar radiation= 1108 W/m^2; average temperature= 28 °C.
b. Each first-order rate constant shows the average value and 95% confidence intervals from linear regression of the individual logarithmic kinetic points.
c. Each half-life shows the average value and the standard deviation calculated from the 95% confidence intervals of the rate constant.

Table 3.4: Effects of Fulvic Acids on UV254 (cm^{-1}) of TOX Samples

Fulvic Acid (mg C/L)	TOCl(Cl_2)	TOCl(NH_2Cl)	TOBr	TOI
0	0.099	0.115	0.106	0.116
2	0.186	0.197	0.195	0.208
5	0.288	0.298	0.292	0.297
10	0.516	0.530	0.521	0.531
20	0.947	0.995	0.981	1.004

Table 3.5: Water quality and TOX formation of real water samples

Water Sample	DOC (mg/L)	SUVA (L/mg/m)	Br^- (mg/L)	Nitrate (mg/L)	Turbidity (NTU)	Cl_2 TOX (μg/L)	NH_2Cl TOX (μg/L)
Big Sioux River	3.4	3.3	0.07	3.16	9.9	NA	NA
Brookings WTP	1.1	1.9	0.01	0.26	0.6	144	41
Brookings WWTP	7.9	3.9	0.04	1.45	1.2	799	235

a. SUVA (specific ultraviolet absorbance) was calculated from UV254 divided by the DOC.
b. NA: not available.

Table 3.6: Effects of Big Sioux River Sample on UV254 of Treated Water and Wastewater Samples

UV254 (cm^{-1})	WWTP (Cl_2)	WWTP (NH_2Cl)	WTP (Cl_2)	WTP (NH_2Cl)
Treated Water	0.199	0.251	0.013	0.018
Treated Water+River Water (Filtered)	0.161	0.187	0.064	0.061
Treated Water+River Water (Unfiltered)	0.479	0.502	0.331	0.369

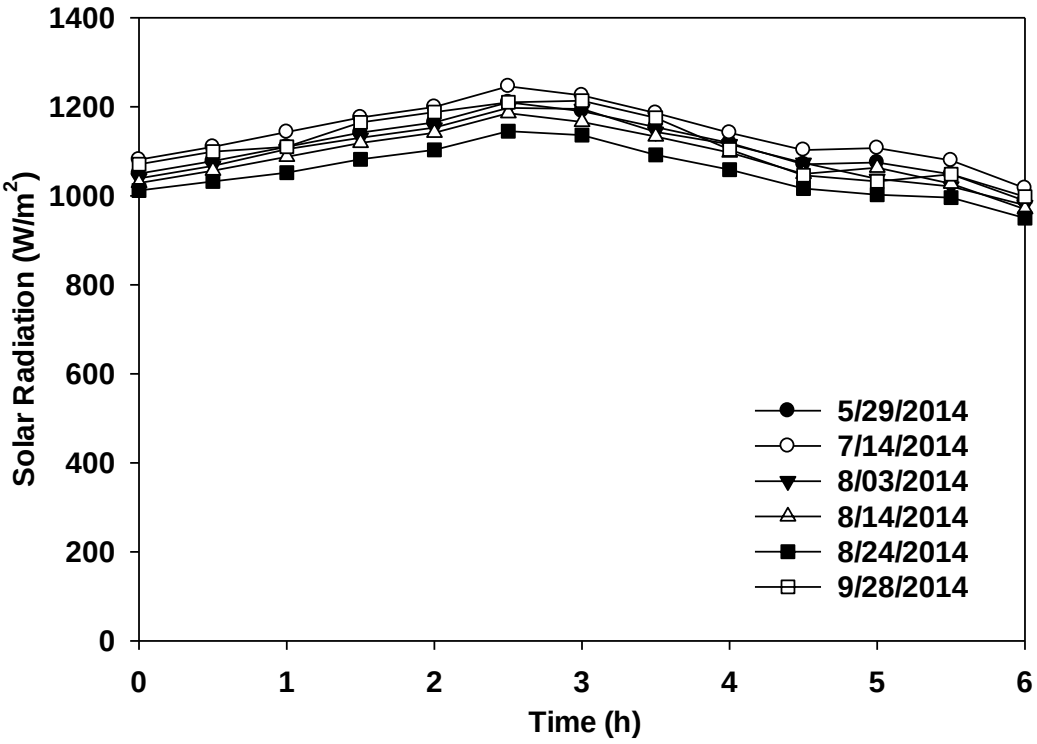

Figure 3.1: Solar radiation intensities for TOX photolysis experiments

Typically sunny days during summer season were selected for this study. The experimental conditions correspond to the surface water body, mid-latitude, clear-sky summer midday conditions with natural variations in solar intensity.

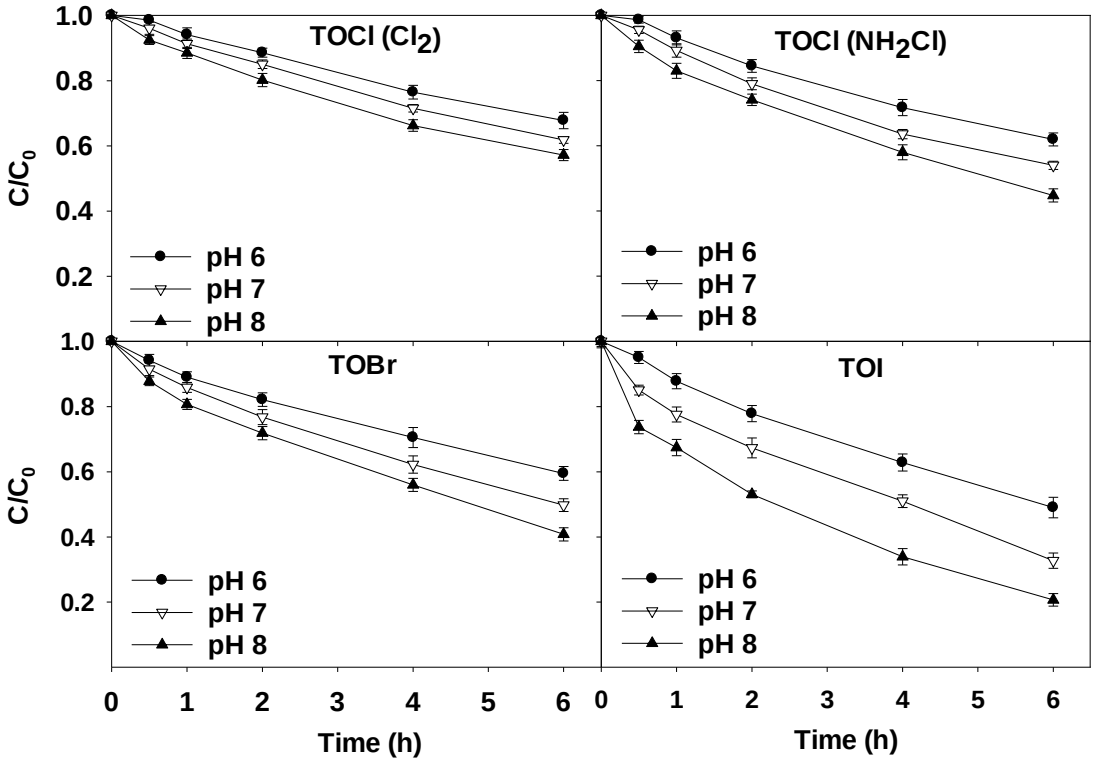

Figure 3.2: Effect of solar irradiation time and pH on the degradation of TOCl, TOBr, and TOI produced by fulvic acid.

(Photolysis experimental conditions: date=05/29/2014, average solar radiation=1108 W/m^2, average temperature =28 ^{o}C. Error bars indicate standard deviations obtained from duplicate experiments.)

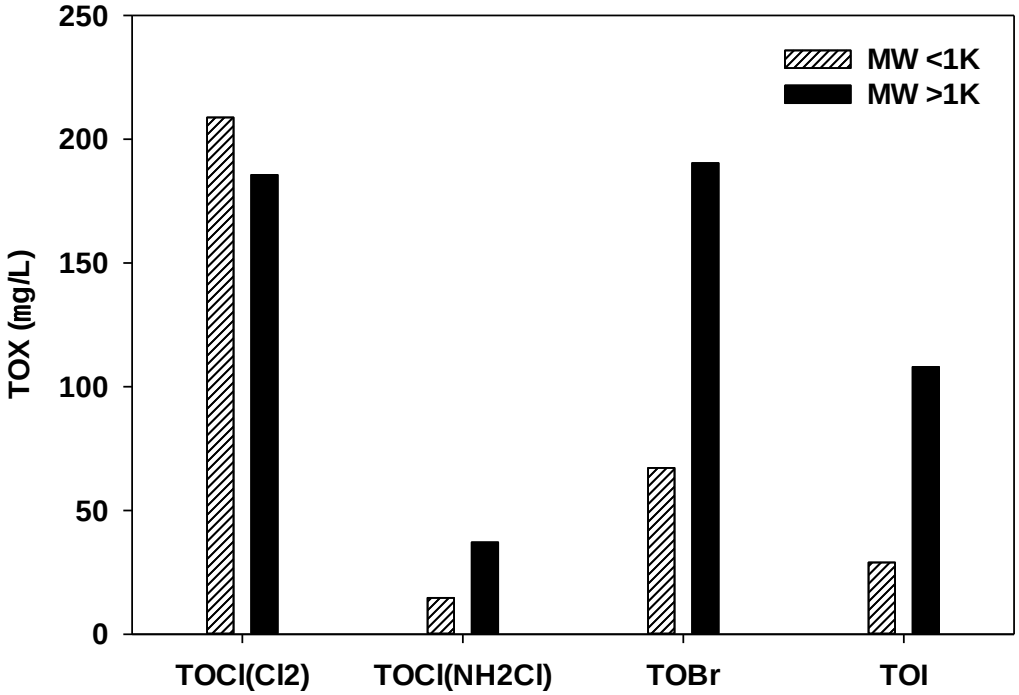

Figure 3.3: MW distribution of TOX formed by fulvic acid

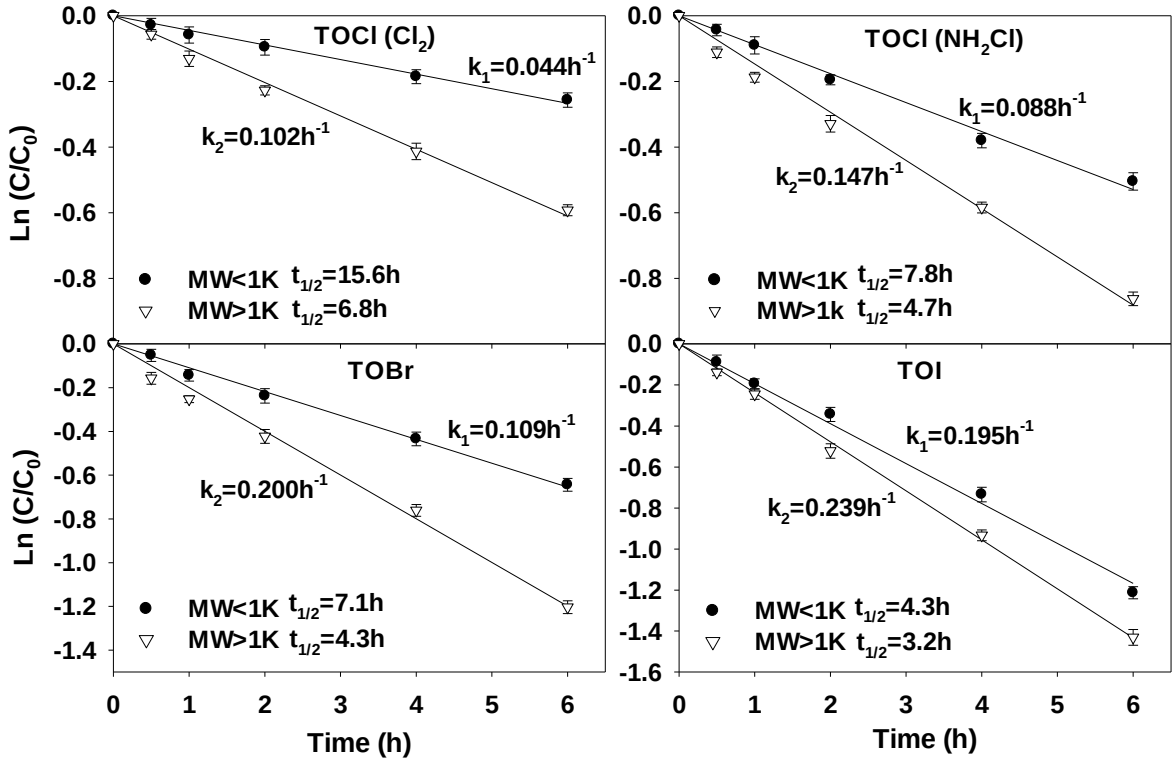

Figure 3.4: Solar photolytic degradation kinetics of high and low MW TOX.

(Photolysis experimental conditions: date=08/03/2014, average solar radiation=1097 W/m^2, average temperature =27 ^{o}C. Error bars indicate standard deviations obtained from duplicate experiments. k=first order rate constant; $t_{1/2}$=half-life.)

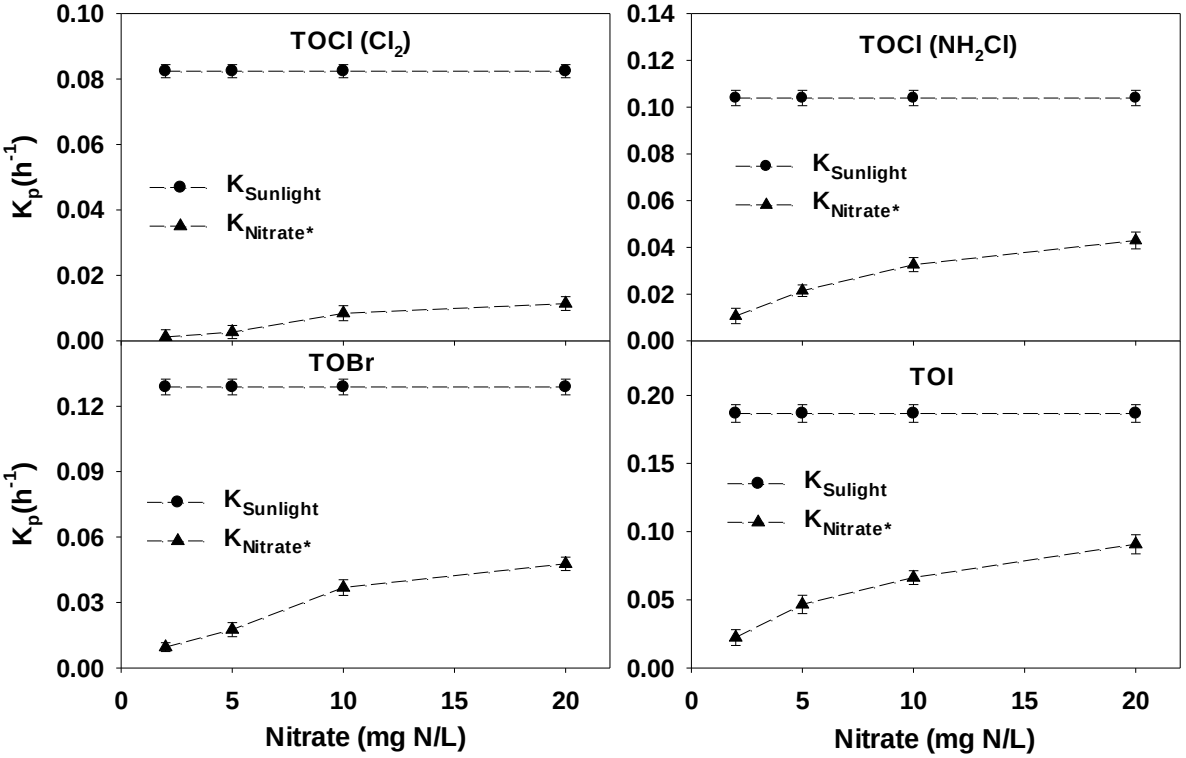

Figure 3.5: Kinetics of nitrate induced indirect photolysis of TOCl, TOBr, and TOI produced by fulvic acid.

(Photolysis experimental conditions: date=07/14/2014, average solar radiation=1140 W/m^2, average temperature =25 ^{o}C. Error bars indicate 95% confidence intervals from linear regression. $k_{sunlight}$ =direct sunlight photolysis rate constant; $k_{nitrate*}$ =nitrate induced indirect photolysis rate constant.)

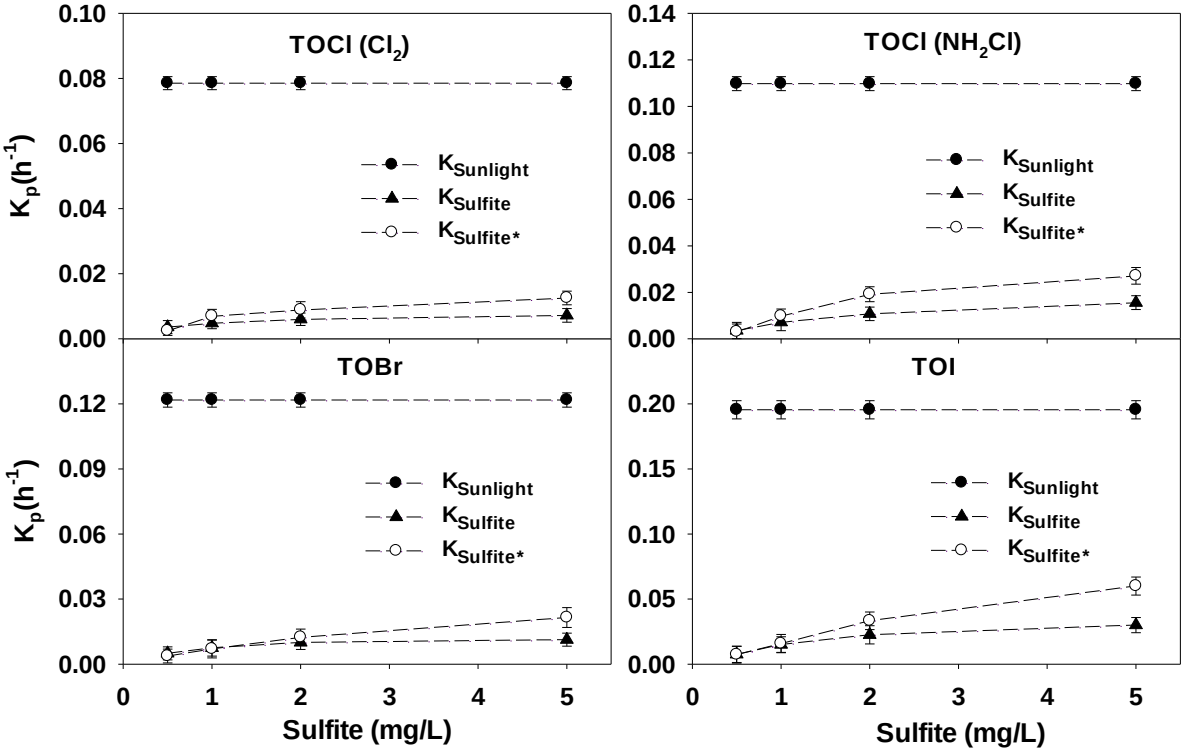

Figure 3.6: Kinetics of sulfite induced indirect photolysis of TOCl, TOBr, and TOI produced by fulvic acid.

(Photolysis experimental conditions: date=08/14/2014, average solar radiation=1087 W/m^2, average temperature =27 ^{o}C. Error bars indicate 95% confidence intervals from linear regression. $k_{sunlight}$ =direct sunlight photolysis rate constant; $k_{sulfite}$=sulfite dehalogenation rate constant in the dark; $k_{sulfite*}$ =sulfite induced indirect photolysis rate constant.)

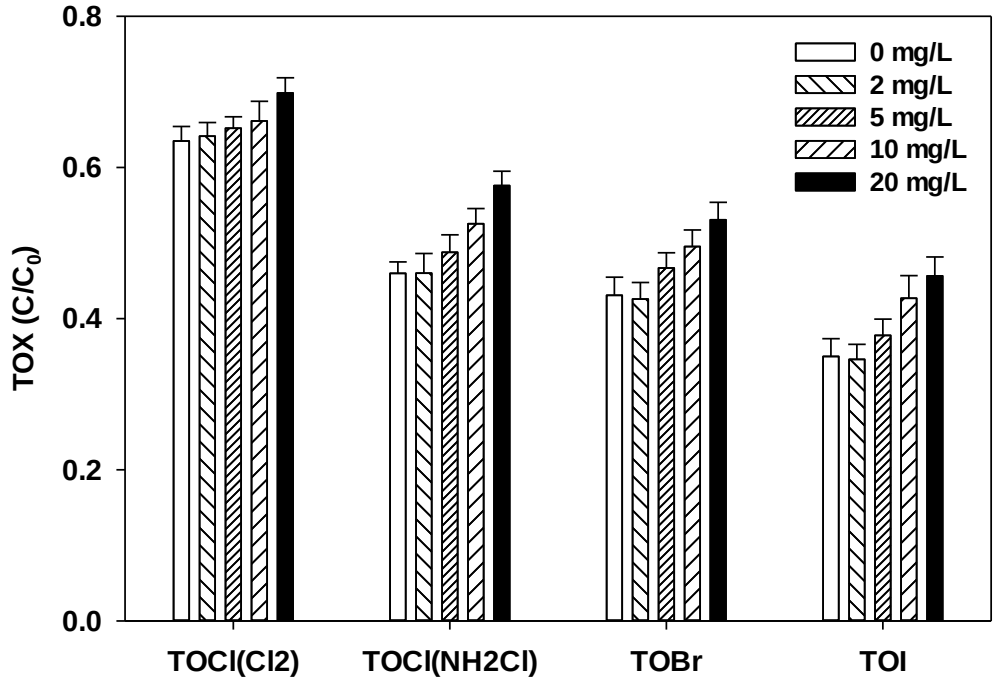

Figure 3.7: Effect of fulvic acid concentrations on solar photodegradation of TOCl, TOBr, and TOI.

(Photolysis experimental conditions: date=08/24/2014, average solar radiation=1052 W/m^2, average temperature =27 ^{o}C, irradiation time=6h. Error bars indicate standard deviations obtained from duplicate experiments.)

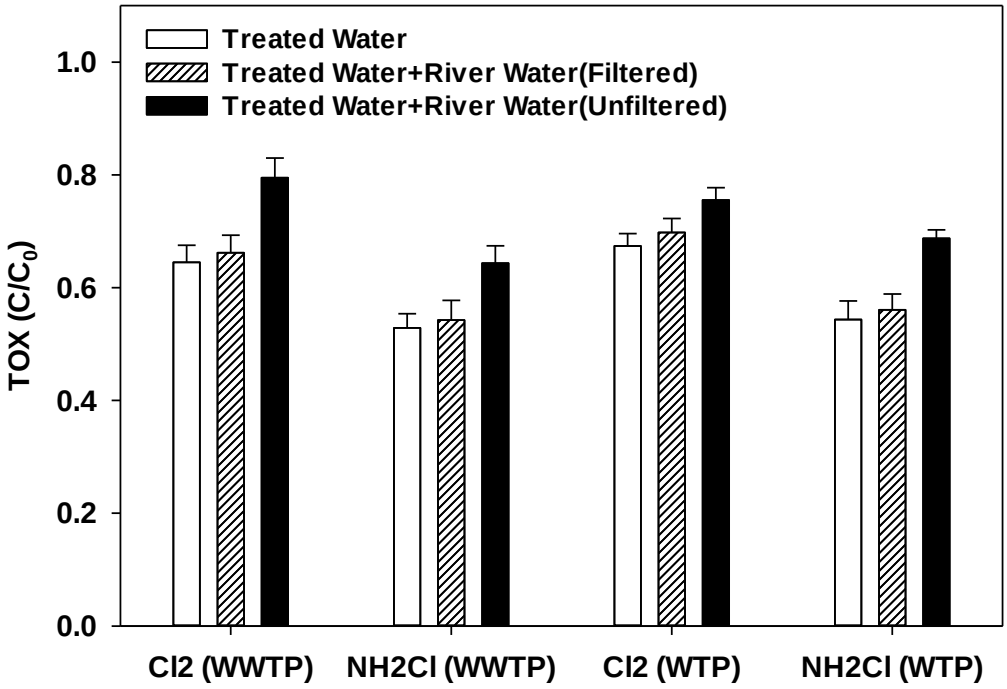

Figure 3.8: Effect of natural water matrix on solar photodegradation of TOX produced by real water and wastewater samples.

(Photolysis experimental conditions: date=09/28/2014, average solar radiation=1112W/m^2, average temperature =26 ^{o}C, irradiation time=6h. Error bars indicate standard deviations obtained from duplicate experiments.)

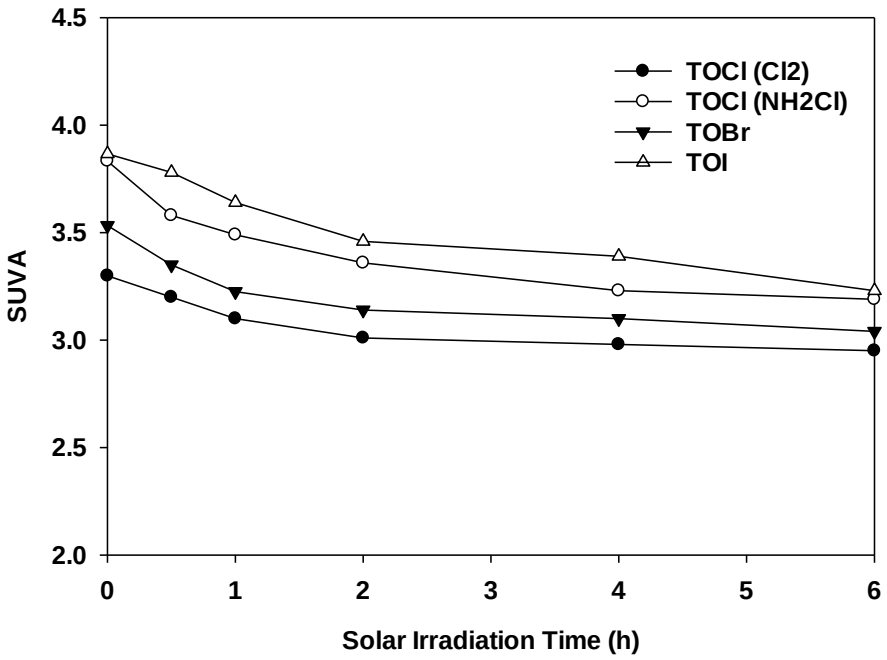

Figure 3.9: SUVA Reductions by Sunlight Irradiation

CHAPTER FOUR
PHOTOLYTIC DEHALOGENATION OF DISINFECTION BYPRODUCTS IN WATER BY NATURAL SUNLIGHT IRRADIATION

Abstract

The aqueous photolysis of halogenated disinfection byproducts (DBPs) by natural sunlight irradiation was studied to determine their photolytic dehalogenation kinetics. Total organic halogen analysis was used to quantify the dehalogenation extents of DBPs during outdoor photolysis experiments. Dichloroacetamide, chloral hydrate, chloroform, dichloroacetonitrile, monochloro-, monobromo-, dichloro-, dibromo-, and trichloroacetic acids were generally resistant to photolytic dehalogenation and showed less than 10% reduction in TOX after 6 h sunlight irradiation. Monoiodoacetic acid, tribromoacetic acid, bromoform, dibromoacetonitrile, and trichloronitromethane showed moderate to high dehalogenation degrees with half-lives of 4.0 to 19.3 h. Diiodoacetic acid, triiodoacetic acid, and iodoform degraded rapidly under the sunlight irradiation and exhibited half-lives of 5.3 to 10.2 min. In general, the photosensitive cleavage of carbon-halogen bonds of DBPs increased with increasing number of halogens (tri- > di- > mono-halogenated) and size of the substituted halogens (I > Br > Cl). Nitrate, nitrite, and pH had little impact on the photodehalogenation of DBPs under typical levels in surface waters. The presence of natural organic matter (NOM) inhibited the photodehalogenation of DBPs by light screening. The NOM inhibiting effects were more pronounced for the fast degrading iodinated DBPs. The results of this study improve our understanding about the photolytic dehalogenation of wastewater-derived DBPs in surface waters during water reuse.

4.1 Introduction

Disinfection is a critical process in the treatment of wastewater to inactivate pathogenic organisms and prevent the spread of waterborne diseases to the environment. Chlorine is the most widely used chemical disinfectant for municipal wastewater disinfection prior to effluent discharge. When chlorine is added to the treated effluent, it can react with effluent organic matter to form a suite of harmful disinfection byproducts (DBPs) including trihalomethanes (THMs), haloacetic acids (HAAs), trihaloacetaldehydes (THAs), haloacetonitriles (HANs), halonitromethanes (HNMs), haloacetamides, nitrosoamines, and others (Mitch and Sedlak, 2002; Yang et al., 2005; Krasner et al., 2009; Huang et al., 2016). It has been shown that the formation of DBPs during wastewater chlorination is highly influenced by the level of wastewater treatment and the concentrations of effluent ammonia. Based on a survey of wastewater treatment plants (WWTPs) in the United States, the DBPs formed at the WWTPs that achieved breakpoint chlorination consisted of high levels of THMs, HAAs, THAs and HANs, which were similar to those detected in drinking waters. For WWTPs disinfected with chloramines, high levels of N-nitrosodimethylamine (NDMA) in the effluent were identified (Krasner et al., 2009).

Municipal WWTP effluents typically contain relatively high levels of bromide and iodide ions compared with drinking water due to wastewater discharges from industrial facilities, hospitals, oil and gas production, and other anthropogenic activities (Krasner et al., 2009; Gong and Zhang, 2013; Hladik et al., 2014; Harkness et al., 2015). The bromide and iodide ions present in the treated effluent can be oxidized by chlorine to bromine and iodine, which subsequently react with effluent organic matter to form

brominated and iodinated DBPs in a way analogues to chlorine (Hua et al., 2006). Bromine and iodine containing DBPs have been shown to be more cytotoxic and genotoxic than their corresponding chlorinated DBPs according to toxicological studies (Richardson et al., 2007; Pals et al., 2013; Yang and Zhang, 2013). This has raised concerns about the potential adverse impacts of these highly toxic DBPs on the aquatic life and human health.

In recent years, treated wastewater has been increasingly used as an alternative water resource to augment drinking water supplies through reclamation, recycling, and reuse. These wastewater recycling and reuse programs are expected to continue to increase in the future to mitigate the water scarcity due to population and economic growth. Indirect potable reuse (intentional and incidental) is one of the water recycling applications that has been in operation in many areas for decades (Rodrigues et al., 2009). During this water reuse practice, DBPs discharged into surface waters from upstream WWTPs can occur in the source water of downstream drinking water treatment plants. Therefore, it is important to understand the fate and transport of DBPs in surface waters to protect aquatic ecosystems and public health during water reuse.

Sunlight photolysis is one of the major natural processes that can affect the concentrations of wastewater-derived DBPs in surface waters. However, limited studies have evaluated the photodegradation of DBPs under natural sunlight irradiation conditions (Lekkas and Nikolaou, 2004; Lifongo et al., 2004; Chen et al., 2010). It has been shown that NDMA and other nitrosamines were highly photosensitive and the half-lives were less than 16 min under natural and simulated sunlight conditions (Plumlee and Reinhard, 2007; Chen et al., 2010). Chlorine and bromine containing HNMs and HANs

typically exhibited higher photolytic losses than THMs and HAAs. Solar photolysis experimental results and quantitative structure-activity relationship (QSAR) analysis suggest that bromine and iodine substituted DBP species were more photosensitive than their chlorinated analogues (Lekkas and Nikolaou, 2004; Chen et al., 2010).

Photodegradation of halogenated DBPs can proceed by stepwise pathways which may result in intermediate products. For example, Castro and Belser (1981) conducted photolysis experiments of trichloronitromethane in aqueous solutions and found that the production rate of chloride was not equal to 3 times that of trichloronitromethane disappearance, suggesting that chlorinated intermediates were produced. The halogenated intermediate and final products from DBP photolysis may still possess toxicity. It is necessary to determine complete dehalogenation extents of DBPs in water by sunlight irradiation in order to provide more accurate information for toxicity and health risk analysis. Moreover, the impact of water matrix (e.g., pH, organic matter, and nitrate) on the solar photolysis of DBPs has not been carefully investigated. Several emerging nitrogenous and iodinated DBPs including dichloroacetamide, iodoform and iodoacids have been identified in treated wastewater effluents. However, information about the impact of natural sunlight irradiation on these highly toxic DBPs is lacking in the literature. The objective of this study was to determine the dehalogenation kinetics of selected chlorine, bromine and iodine containing DBPs under natural sunlight irradiation conditions. Total organic halogen (TOX) was used as an analytical tool to quantify the dehalogenation extents of selected DBPs during outdoor photolysis experiments. The impact of pH, dissolved organic matter, nitrate, and nitrite on solar photolysis of DBPs was also evaluated. The results of this study provide quantitative information about the

dehalogenation kinetics of DBPs including several emerging nitrogenous and iodinated compounds under the natural sunlight irradiation, which can help evaluate the fate of chlorinated, brominated and iodinated DBPs in surface waters.

4.2 Experimental Methods

4.2.1 Preparation of DBP Samples

A total of 17 DBPs were selected for the solar photolysis experiments. These DBPs included three THMs (chlororform, bromoform, iodoform), nine HAAs (monochloro-, monobromo-, monoiodo-, dichloro-, dibromo-, diiodo-, trichloro-, tribromo-, and triiodoacetic acid (MCAA, MBAA, MIAA, DCAA, DBAA, DIAA, TCAA, TBAA, and TIAA, respectively)), two HANs (dichloro- and dibromoacetonitrile (DCAN, and DBAN)), trichloronitromethane (TCNM), chloral hydrate (CH), and dichloroacetamide (DCAcAm). DIAA (90%), and TIAA (90%) were obtained from Toronto Research Chemicals, Inc. (Toronto, Ontario). All other DBPs were purchased from Sigma Aldrich (St Luis, MO). Each DBP was dissolved in ultrapure water at an initial concentration of 300 ± 10 µg/L as Cl, Br, or I for chlorinated, brominated, and iodinated compounds, respectively, before photolysis experiments. Bromoform, chloroform, DBAN, DCAN, iodoform, and TCNM have low solubility in water. Stock solutions of these DBPs in acetone were made before diluting in ultrapure water. The Suwannee River humic acid (SRHA) and the Pony Lake fulvic acid (PLFA) were obtained from the International Humic Substances Society. These natural organic matter (NOM) extracts were used to spike the DBP solutions to investigate the NOM impact on photolysis. Potassium nitrate and potassium nitrite (American Chemical Society reagent grade) were purchased from Fisher Scientific (Fairlawn, NJ) and used as nitrate and

nitrite sources for the photolysis experiments. All solutions used in this study were prepared with ultrapure water (18 MΩ-cm) produced by a Barnstead NANOpure system.

4.2.2 Natural Solar Photolysis Experiments

Natural solar photolysis experiments were performed using 60 mL quartz tubes with an outside diameter of 25 mm and a length of 150 mm. The thickness of the tube wall was 1.5 mm. The quartz tubes were capped to prevent the volatilization and evaporation of each DBP sample during the photolysis experiments. The sample tubes were placed on fabricated platforms at a 30^{o} angle. The outdoor solar photolysis experiments were conducted between June and August 2015, in an open space adjacent to the Water and Environmental Engineering Research Center in Brookings, SD, USA (44°18'53.5"N, 96°47'09.7"W). Each set of photolysis experiments was started at 11:30 am on the testing day and extended for a total of 6 h of sunlight exposure. The solar radiation intensity (W/m^2) was recorded on-site every 30 min using a photometer (Seaward 396A916, Tampa, FL). Table 4.1 presents the weather conditions for the photolysis experiments. The average solar radiation intensities varied between 1087 and 1139 W/m^2 and the average temperatures varied between 20 and 22 ^{o}C during these photolysis experiments. The cloud cover was also monitored throughout the experiments by visual observation and a photometer, and the duration of cloud cover during each photolysis experiment was less than 10 min. These DBP photolysis conditions correspond to the surface water body, mid-latitude, clear-sky summer midday conditions with natural variations in solar intensity. Detailed information about the variation of solar intensities during the photolysis experiments is reported in Figure 4.1.

A total of four sets of outdoor photolysis experiments were performed to evaluate the impact of time, pH, nitrate/nitrite, and NOM on photolytic dehalogenation of selected DBPs. The goal of the first set of experiments was to determine the photolytic dehalogenation kinetics of each DBP. Preliminary tests showed that DIAA, TIAA and iodoform degraded much faster than other DBPs. These three iodinated DBP samples were subject to solar irradiation for 0, 2, 5, 15, and 30 min while other DBP samples were subject to solar irradiation for 0, 0.5, 1, 2, 4, and 6 h at pH 7. The TOX concentrations of DBP samples at different solar irradiation time intervals were determined. Based on the results of the first set of experiments, seven DBP species (bromoform, iodoform, MIAA, DIAA, TIAA, DBAN, and TCNM) were selected for subsequent photolysis experiments. During the second set of experiments, DIAA, TIAA, iodoform were subject to solar irradiation for 15 min and others were subject to solar irradiation for 6 h for three pH values (6, 7 and 8). Phosphate buffers (1 mM) were used to adjust the pH values of each sample. During the last two sets of DBP photolysis experiments, each sample was spiked with different levels of nitrate (0-20 mg/L), nitrite (0-5 mg/L), SRHA (0-20 mg/L as dissolved organic carbon (DOC)), or PLFA (0-20 mg/L DOC) separately to investigate the impact of these water quality parameters on DBP photodehalogenation by sunlight. The selected concentrations cover a broad range of those parameters reported in surface waters (Philips et al., 2002; Camargo et al., 2005; Evans et al. 2005). After being dosed with each of these chemicals, DIAA, TIAA, iodoform samples were subject to solar irradiation for 15 min and others were subject to solar irradiation for 6 h at pH 7. All DBP photolysis samples were collected for the measurement of TOX concentrations.

All solar irradiation experiments were conducted in duplicate. Dark control experiments were also performed simultaneously for each set of samples. The dark control sample tubes were wrapped with aluminum foil, and placed in a box adjacent to the solar photolysis platforms. The control samples were taken at different time intervals to determine the possible DBP dehalogenation kinetics in the dark.

4.2.3 Analytical Methods

The DOC concentrations in the SRHA and PLFA stock solutions were determined with a Shimadzu TOC-5000 Analyzer (Shimadzu Corp., Kyoto, Japan) according to Standard Method 5310 B (APHA et al., 2012). The UV absorbance (UV254) of the DBP solution was measured by a Hach DR4000U spectrophotometer Hach, Loveland, CO). The TOX samples were acidified to pH 2 by concentrated nitric acid immediately after sampling and stored at 4 ^{o}C before the analysis. The TOX was determined by an adsorption-pyrolysis-titration method with a Mitsubishi TOX-100 Analyzer (Cosa Xentaur Inc., Norwood, NJ). The method was based on standard method 5320 B with minor modifications (Hua and Reckhow, 2006; APHA et al., 2012). TOX recovery tests were performed on DBPs including bromoform, iodoform, MCAA, MBAA, MIAA, DCAA, DBAA, TCAA, TBAA, DCAN, DBAN, CH, DCAcAm, and TCNM. The recoveries of these DBPs by the TOX method were between 96 and 103%.

4.3 Results and discussion

4.3.1 Dehalogenation Kinetics of DBPs by Natural Sunlight Irradiation

Figure 4.2 shows ratios of the TOX concentrations of each DBP at different sunlight exposure times (C) to the initial concentration (C_0). The DBP stability in the dark was also evaluated through the dark control experiments. The average variations of

TOX for each sample was less than 4% during incubation in the absence of sunlight irradiation (Table 4.2), suggesting that the dehalogenation of these DBPs in the dark was insignificant under the conditions of this study. To facilitate the discussion of the photolysis results, the selected DBPs were classified into three groups: neutral compounds (DCAcAm, CH, chloroform, DCAN, DBAN, bromoform, and TCNM), acidic compounds (MCAA, MBAA, DCAA, DBAA, TCAA, MIAA, and TBAA), and fast degrading compounds (DIAA, TIAA and iodoform). Among the neutral compounds, DCAcAm (2.6%), CH (4.1%), chloroform (6.3%), and DCAN (9.4%) showed dehalogenation degrees less than 10% after 6 h exposure to natural sunlight irradiation. Haloacetamides are a class of emerging halogenated nitrogenous DBPs, which were two orders of magnitude more cytotoxic that HAAs (Plewa et al., 2008). The photolysis results indicate that the C-Cl bounds in DCAcAm were resistant to cleavage by solar photolysis and this highly toxic emerging DBP may be persistent in surface waters under sunlight irradiation. Chloroform, CH, and DCAN also showed limited reductions in TOX concentrations during the sunlight irradiation experiments, suggesting that solar photolysis may not be a major dehalogenation pathway for these compounds in the natural environment. Chen et al. (2010) reported a 46% of reduction in DCAN concentrations after 6 h irradiation under the natural sunlight. This may be attributed to the hydrolysis of DCAN forming DCAcAm or that the photolysis of DCAN may produce chlorinated products without substantial loss of chlorine.

Appreciable dehalogenation extents after 6 h of solar photolysis were observed for DBAN (38.3%) and bromoform (43.4%), which were higher than that of DCAN and chloroform. This is consistent with structure-activity relationship expectations that

bromine is more photosensitive and has a higher leaving tendency than chlorine (Chen et al, 2010). Among the selected neutral compounds, TCNM was the most photosensitive DBP and decomposed rapidly by sunlight. A loss of 66.9% of chlorine in TCNM was resulted after 6 h exposure to sunlight irradiation. Rapid degradation of TCNM by sunlight was also observed in other studies (Castro and Belser, 1981; Chen et al., 2010). Homolytic cleavage of C-Cl or C-N bonds in TCNM has been proposed for the photolysis of TCNM by UV or sunlight irradiation (Castro and Bleser, 1981; Fang et al., 2013). TCNM showed a much higher dehalogenation degree than chloroform, CH, DCAN and DCAcAm, which may be attributed to the electronic effect of different functional groups substituted on the α-carbon atom. It is seems that the presence of a nitro functional group substantially enhanced the photolytic loss of chlorine from the carbon-halogen bonds compared to other functional groups. It can be inferred from this result that TCNM could be dissipated quickly in the aquatic environment with proper exposure to sunlight.

Chlorine and bromine containing HAAs were generally resistant to solar photolysis with the exception of TBAA. MCAA (2.5%), MBAA (3.9%), DCAA (5.8%), DBAA (7.0%), and TCAA (7.6%) exhibited dehalogenation degrees less than 10% after 6 h exposure to sunlight irradiation. These HAAs are expected to be relatively persistent under the sunlight in the natural environment (Lifongo et al., 2004). Increased photodehalogenation rates were observed for MIAA and TBAA, and the reductions in TOX concentrations were 18.5% and 22.5% for these two compounds after 6 h solar photolysis. Although MIAA was more photosensitive than MCAA and MBAA, the majority of initial organic iodine in the MIAA sample remained after 6 h under the

sunlight irradiation. MIAA is one of the most toxic and genotoxic DBPs in mammalian cells reported in the literature (Plewa et al., 2004). The occurrence of MIAA in water reuse and its impact on aquatic life and human health should be further evaluated.

Three iodinated DBPs: DIAA, TIAA and iodoform were identified as fast degrading compounds under the sunlight irradiation during this study. These iodinated compounds exhibited an initial rapid dehalogenation phase within the first 15 min, followed by a more steadily decreasing phase during the second 15 min. The TOX concentrations of the three DBPs reduced by 33.7, 43.5, and 53.6%, respectively, for DIAA, TIAA and iodoform after 5 min exposure to sunlight. The dehalogenation degrees of these compounds increased to 86.0, 91.0, and 98.1% when the sunlight exposure time increased to 30 min. These results indicate that the three iodinated DBPs were highly susceptible to solar photolysis and the C-I bonds in these compounds were quickly cleaved by sunlight. Natural sunlight irradiation could be a very effective process to reduce the concentrations of these di- and triiodinated DBPs in surface waters. The DBP solar photolysis results suggest that the photosensitive cleavage of carbon-halogen bonds increased with increasing number of halogens (tri- > di- > mono-halogenated) and size of the substituted halogens (I > Br > Cl). The effects of halogen species on DBP photodehalogenation can be explained in part by the carbon-halogen dissociation energies: 397, 280, 209 kJ/mol for C-Cl, C-Br, and C-I bonds, respectively (Weast et al., 1986). In addition to the bond dissociation energies, the steric and electronic effects of halogen substituents may also play an important role in the photosensitive cleavage of carbon-halogen bonds. DBPs with higher numbers of halogen atoms exhibited higher

photolytic dehalogenation degrees, which can be attributed to the increased electron withdrawing effects (Fang et al., 2013).

Table 4.3 summarizes the pseudo-first-order rate constants (kp), calculated half-lives, and linear regression coefficients (R^2) for solar photolysis of the DBPs that showed higher than 10% reductions in TOX concentrations at the end of the experiments. The R^2 values were all higher than 0.98, suggesting that the photolytic dehalogenation of these DBPs could be described by the first-order kinetics. The half-lives for halogen in TCNM, bromoform, DBAN, TBAA, and MIAA were 4.0, 7.3, 8.7, 15.1 and 19.3 h, respectively, under the sunlight irradiation. These DBPs, especially TCNM could be decomposed by natural sunlight within practical exposure times. The half-lives for iodine in iodoform, TIAA, and DIAA were 5.3, 8.5, and 10.2 min, respectively. Iodoform was the most photosensitive DBP identified in this study. The solar photolysis rates and half-lives of these iodinated DBPs were similar to those of NDMA and other nitrosamines (Plumlee and Reinhard, 2007; Chen et al., 2010). These results suggest that these three iodinated DBPs and potentially other iodine containing compounds could be dissipated by natural sunlight within very short exposure times. Xiao et al. (2014) performed a laboratory evaluation of the photodegradation of 6 iodinated THMs under UV irradiation at 254 nm and the results showed that iodinated THMs underwent rapid photodegradation process with half-lives in the range of 1.2-6.9 min. Jones and Carpenter (2005) investigated the solar photolysis of reactive volatile organic iodine compounds. The half-lives of CH_2I_2 under natural sunlight were 9.2-9.6 min in water and 18-21 min in seawater. The results of these studies suggest that organic iodine compounds are highly photosensitive, and natural sunlight and UV light can effectively cleave carbon-iodine bonds. The half-lives

for iodoform and TIAA obtained through this study were different from the expectations of the QSAR analysis, which suggested 8 min and 11 s for iodoform and TIAA under natural sunlight (Chen et al., 2010). The QSAR models are quantitative regression methods that attempt to relate chemical structure to activity. This tool has been used to correlate the hydrolysis and photolysis rate constants of DBPs to the steric and electronic effects of substituted halogens and other functional groups (Zhang and Minear, 2002; Chen et al., 2010). The QSAR generally assumes a linear relationship between molecular structure and reactivity. It is possible that the structure-activity relationships for photosensitive cleavage of carbon-halogen bonds are at least in part nonlinear in nature. The sunlight photolysis experimental conditions may also contribute to the distinction between the experimental results and the QSAR predictions. Aside from the different solar intensities and DBP concentrations, Chen et al. (2010) focused on the degradation of parent compounds whereas this study focused on the dehalogenation of DBPs. Therefore, although QSAR analysis is useful for predicting the chemical behaviors of a large number of chemical compounds, it cannot replace actual solar photolysis experiments for precise kinetic determination.

4.3.2 Effect of Nitrate, Nitrite and pH on Photolytic Dehalogenation of DBPs by Natural Sunlight

Nitrate is a common photosensitizer in surface waters. Sunlight excitation of nitrate ions can lead to the formation of $^{\bullet}OH$ radical, one of the principal intermediate in natural water photochemical processes. Various nitrogen reactive species ($NO^{\bullet}$, $NO_2^{\bullet}$, etc.) can also be produced by nitrate photolysis (Mack and Bolton, 1999). Nitrate induced indirect photolysis has been identified as an important degradation pathway for a large number of organic compounds (Mack and Bolton, 1999). Figure 4.3 presents the

dehalogenation extents of selected DBPs by sunlight irradiation at different nitrate concentrations. The added nitrate affected the solar photolysis of MIAA, DBAN, bromoform and TCNM to varying degrees. The photolytic loss of halogen of these DBPs after 6 h sunlight exposure varied by -1.0 to 5.8 percentage points in the presence of 5 to 10 mg/L of nitrate. This indicates that nitrate induced indirect photolysis had limited impact on the photolysis of these DBPs when the nitrate concentration was less than 10 mg/L. Enhanced dehalogenation of MIAA, DBAN, and bromoform was observed when the nitrate concentration increased to 20 mg/L. The dehalogenation extents increased by 14.1, 10.4, and 11.8 percentage points for MIAA, DBAN, and bromoform, respectively. TCNM photolysis was not substantially affected at this level of nitrate since only an increase of 3.7 percentage points was observed.

Nitrate induced indirect photolysis was not observed for DIAA, TIAA and iodoform within 15 min of sunlight irradiation. The TOX concentrations of these compounds at different levels of nitrate varied by 0 to 1.9 percentage points. The sunlight irradiation experiments of di- and triiodinated DBPs suggest that the presence of •OH and other photochemically produced reactive species by nitrate did not enhance the photolysis of these compounds through an indirect photosensitization. It is likely that the reaction rates of •OH and these iodinated DBPs could not compete with the fast direct photodehalogenation rates by sunlight irradiation. Second order reaction rate constants of hydroxyl radicals with iodoform, DBAN, bromoform, and TCNM have been reported to be 8.9×10^9, 2.8×10^9, 1.5×10^8, and 4.97×10^7 $M^{-1}S^{-1}$, respectively, in the literature (Mezyk et al., 2006; Cole et al., 2007; Xiao et al., 2015; Kiattisaksiri et al., 2016). Similar hydroxyl radical reactions rate constants were also reported for THMs ($0.7 \times 10^7 – 1.5 \times$

10^8 $M^{-1}S^{-1}$) and chlorinated HAAs ($6 \times 10^7 – 1.0 \times 10^8$ $M^{-1}S^{-1}$) (Jo et al., 2011). The steady state •OH concentrations in several natural waters have been estimated to be in the range of $2.5 \times 10^{-17} – 1.0 \times 10^{-15}$ M as a result of nitrate photolysis for noon, midsummer sun at the surface of water bodies (Brezonik and Fulkerson-Brekken, 1998). The half-lives of iodoform, DBAN, bromoform, and TCNM in presence of 1.0×10^{-15} M •OH are expected to range from 3 to 161 d according to the reported rate constants. Therefore, the contribution of nitrate induced indirect photolysis to DBP degradation is likely insignificant based on the results of this study and the reported hydroxyl radical reaction rate constants.

Figure 4.4 shows the effect of nitrite and pH on the photolytic dehalogenation of DBPs by sunlight irradiation. Similar to nitrate, nitrite ions are also photosensitizers which can form •OH radical and nitrogen reactive species under natural sunlight (Mack and Bolton, 1999). However, the added nitrite in the range of 1 to 5 mg/L did not affect the dehalogentation rates of the selected DBPs by sunlight irradiation. Figure 4.4 also shows that the dehalogenation rates of each DBP was not affected by the pH values in the range of 6 to 8. Wu et al. (2001) reported that the pH in the range of 1.1-11.2 did not affect the photodegradation of TCAA by UV light. Fang et al. (2013) showed that the UV photolysis rates of TCNM changed little with changing pH due to the lack of acid functionality. However, other HNMs (bromo-, dibromo-, and dichloro-nitromethanes) exhibited increased photolysis rates when increasing pH from 4 to 9. It was thought that the deprotonated forms of these HNMs (pKa 6.0-7.6) increased UV absorption thereby enhancing the photodegradation. Among the selected DBPs, the chemical structure of TCNM is not affect by the pH values. The pKa value of MIAA is 3.12 (Plewa et al.,

2004), and DIAA and TIAA are expected to have lower pKa values due to higher electron withdrawing effects. Bromoform has a pKa value of 11.8 (Scharlin, 1986). High pKa values are also expected for DBAN and iodoform. The pH range tested in this study would have little impact on the chemical forms of these DBPs, which may explain the observed pH effects on solar photolysis rates. The results in Figures 4.2 and 4.3 suggest that nitrate, nitrite, and pH would have limited effects on the photodehalogenation of DBPs under typical levels in surface waters. Abusallout and Hua (2016a) showed that the sunlight photodehalogenation rates of the TOX compounds formed by fulvic acid increased by 49 to 133% when increasing pH to 8 from 6. This indicates that the unidentified and known DBPs behave differently regarding the pH effect on solar photolysis.

4.3.3 Effect of NOM on Photolytic Dehalogenation of DBPs by Natural Sunlight

Indirect photolysis by NOM is an important mechanism for attenuation of organic contaminants in surface waters (Wenk et al., 2011). Sunlight irradiation of NOM photosensitizers can produce excited triplet states of NOM. Triplet-induced phototransformation has been shown to increase the degradation rates of many organic contaminants under sunlight irradiation. At the same time, NOM also contains a broad diversity of chromophores that are capable of absorbing light. The light screening effect of NOM may negatively impact the efficiency of direct photolysis. Figure 4.5 presents the effect of PLFA and SRHA on the photolytic dehalogenation of DBPs by natural sunlight. The SRHA is an allochthonous NOM derived mainly from the decay of wood materials whereas PLFA is an autochthonous NOM derived from phytoplankton sources. These two organic extracts represent two different types of NOM and therefore reflect a

great extent of variability in the effects of surface water NOM on solar photolysis. As shown in Figure 4.5, NOM induced indirect photodehalogenation of these DBPs was not observed. The dehalogenation extents of each DBP decreased with spiked NOM during the photolysis experiments. The reduced photolytic dehalogenation of DBPs in the presence of NOM can be attributed to the competitive sunlight absorption by NOM molecules. It is possible that halogenated DBPs are not reactive with triplet NOM produced from photosensitized reactions or that the roles of SRHA and PLFA as inhibitors of DBP photolysis exceed their roles as photosensitizers.

The inhibiting effects on photodehalogenation of DBPs by these two NOM products were similar among MIAA, DBAN, and bromoform. The dehalogenation extents of these DBPs decreased by 5.6-7.2%, 7.9-13.6%, 9.1-15.4%, and 12.6-22.9% for samples spiked with 10 mg/L PLFA, 10 mg/L SRHA, 20 mg/L PLFA, and 20 mg/L SRHA, respectively. Increased NOM inhibiting effects were observed for TCNM and the dehalogenation degrees after 6 h sunlight exposure decreased by 16.3 to 55.5% for the two NOM products at two concentrations. The PLFA and SRHA exhibited higher inhibiting effects on the three fast degrading iodinated DBPs. When spiked with 10 mg/L PLFA, the photolytic dehalogenation extents after 15 min sunlight irradiation reduced by 18.4, 26.7, and 68.6% for DIAA, TIAA, and iodoform, respectively. The corresponding reduction rates increased to 58.7, 89.0, and 174.7% when the samples were spiked with 20 mg/L SRHA.

In general, the two NOM products had higher inhibiting effects on the fast degrading DBPs than the slow degrading DBPs under sunlight irradiation. The spiked NOM caused the largest reductions in solar photolysis efficiency of iodoform, which was

also the most photosensitive DBP identified in this study. The two types of NOM extract also exhibited different inhibiting efficiencies in the order of PLFA(10 mg/L) < PLFA (20 mg/L) ≅ SRHA (10 mg/L) < SRHA (20 mg/L). The SRHA at 10 mg/L caused similar reductions in the DBP photodehalogenation efficiency to the PLFA at 20 mg/L. The reduced DBP photodehalogenation by NOM is likely attributable to the light screening effects of the organic molecules. The UV254 of each sample was used to quantify the light absorbing effects of the two NOM products. Table 4.4 shows the UV254 values of DBP solutions with different concentrations of spiked NOM. The UV254 of the DBP solutions without NOM ranged from 0.015 cm^{-1} (MIAA) to 0.081 cm^{-1}(iodoform). The order of the UV254 values of DBP solutions positively correlated with the order of the dehalogenation rates by sunlight irradiation. Therefore, the UV254 value of each DBP solution may be used as an indicator for the photodehalogenation potential by solar photolysis. The spiked NOM caused substantial increases in the UV254 for all DBP samples. The UV254 varied from 0.215 to 0.277 cm^{-1} for the solutions spiked with 10 mg/L PLFA. When 20 mg/L PLFA was added to each sample, the UV254 increased to 0.521 to 0.582 cm^{-1}, which were similar to those samples fortified with 10 mg/L SRHA (0.522 to 0.572 cm^{-1}). This result suggests that 20 mg/L PLFA and 10 mg/L SRHA led to similar light screening effects on the DBPs samples at 254 nm. The SRHA organic compounds had much higher UV absorbing capacity than the PLFA organic compounds. This may explain the similar reductions in DBP photodehalogenation efficiencies caused by 20 mg/L PLFA and 10 mg/L SRHA. The addition of 20 mg/L SRHA resulted in the highest range of UV254 absorbance (0.943 to 1.055 cm^{-1}), which also led to the most reductions on DBP dehalogenation extents. The light screening

ability of NOM, as evidenced by the UV254 value can be used to estimate the potential impact of NOM on solar photolysis of DBPs.

4.3.4 Implications on Water Reuse Practices

Water recycling and reuse have been recognized as effective and sustainable water management practices to mitigate water shortage due to population growth and increase climate change resilience of water infrastructure. The potential impacts of contaminants in the treated wastewater effluent on the natural environment and human health should be carefully evaluated to avoid the unintended consequences of water reuse practices. The results of this study showed that different groups of DBPs exhibited distinctly different susceptibility to photolytic dehalogenation by natural sunlight irradiation. The photodehalogenation percentages and rate constants of different DBPs obtained through this study can be used to evaluate their fates in surface waters under sunlight irradiation. Direct photolysis was found to be the primary photodehalogenation pathway during the solar photolysis experiments. The contribution of indirect photolysis induced by nitrate, nitrite, and NOM to DBP photodehalogenation was insignificant compared to direct photolysis. Proper exposure of treated effluent to sunlight in rivers, streams and reservoirs may enhance the degradation of DBPs during water reuse.

Iodinated DBPs are a group of highly toxic emerging contaminants in water and wastewater. Inorganic and organic precursors to the formation of iodinated DBPs include naturally occurring iodide, iodine containing chemicals from wastewater discharge, and others. The exploration and production of oil and gas has produced large volumes of produced waters that are high in iodide and bromide concentrations. High levels of iodinated DBPs can be formed when produced water brines are chlorinated (Hladik et al.,

2014; Harkness et al., 2015). Chemicals compounds widely used in medical imaging are an important group of precursors to iodinated DBPs in hospital wastewaters (Duirk et al., 2011). The results of solar photolysis experiments showed that DIAA, TIAA and iodoform were highly photosensitive and their half-lives were less than 11 min under natural sunlight irradiation. These iodine containing DBPs can be effectively decomposed by natural sunlight. This indicates that although iodinated DBPs may be more toxic than chlorine and bromine containing DBPs, they may have much shorter lives in the aquatic environment under sunlight irradiation. The fast photodehalogenation of iodinated DBPs also suggests that engineered opportunities should be explored to develop treatment processes (e.g., open channels or reservoirs) using solar energy to reduce or eliminate certain iodinated DBPs in the treated effluent during water reuse.

The DBP photolytic dehalogenation rates obtained in this study correspond to the surface water body, mid-latitude, clear-sky summer midday conditions. Attenuation of pollutants by natural sunlight in surface waters depends on actual solar irradiation intensity, the water depth, the light screening of the water constituents, and physical and biological conditions of the stream. The water depth will substantially affect the photolysis of DBPs due to the reduced light penetration. Plumlee and Reinhard (2007) used SMARTS (Simple Model for the Atmospheric Radiative Transfer of Sunshine) to model the NDMA photodecay rates for midday solar irradiance in a mid-latitude zone in surface water with intermediate light screening and a depth of 1 m. The half-life of NDMA at 1 m water depth increased by a factor of 26 compared to the water surface. When the same factor is applied to the photolysis of iodinated DBPs, one comes up with estimated half-lives in the range of 2.3-4.4 h for iodoform, TIAA and DIAA at 1 m water

depth. Other researchers have used variable factors to account for the diurnal variation, partial cloud cover, the mixing in a water layer when estimating the photolysis rates of organic contaminants in natural water systems (Bahnmuller et al., 2014). Further studies are necessary to evaluate the photodehalogenation of DBPs in real surface water bodies.

4.4 Conclusions

The objective of this research was to determine the dehalogenation kinetics of selected chlorine, bromine and iodine containing DBPs under natural sunlight irradiation conditions. TOX analysis was used to quantify complete dehalogenation extents of DBPs by sunlight irradiation using outdoor photolysis experiments. DCAcAm (2.6%), CH (4.1%), chloroform (6.3%), and DCAN (9.4%) were generally resistant to photolytic dehalogenation by sunlight, and showed dehalogenation degrees less than 10% after 6 h exposure to natural sunlight irradiation. MIAA, TBAA, bromoform, DBAN, and TCNM exhibited moderate to high dehalogenation degrees with half-lives of 4.0 to 19.3 h under sunlight irradiation. DIAA, TIAA and iodoform degraded rapidly by sunlight irradiation and exhibited half-lives of 5.3 to 10.2 min. In general, the photosensitive cleavage of carbon-halogen bonds of DBPs increased with increasing number of halogens (tri- > di- > mono-halogenated) and size of the substituted halogens (I > Br > Cl). Natural sunlight irradiation can be a highly effective process to decompose certain iodinated DBPs in surface waters.

The solar photolysis experiments showed that the pH values in the range of 6-8 and nitrite in the levels of 0-5 mg/L did not affect the photodehalogenation of DBPs. Nitrate did not substantially affect the photodehalogenation of selected DBPs when the concentration was less than 10 mg/L. The dehalogenation degrees of MIAA, DBAN, and

bromoform increased by 11-14 percentage points after 6 h sunlight irradiation in the presence of 20 mg/L nitrate. Overall, nitrate, nitrite, and pH had little impact on the photodehalogenation of DBPs under typical levels in surface waters. Direct photolysis was the primary photodehalogenation pathway for the DBPs. The presence of PLFA and SRHA NOM in the solution inhibited the photodehalogenation of DBPs by light screening. The NOM inhibiting effects were more pronounced for the fasting degrading iodinated DBPs.

Table 4.1: Weather conditions for DBPs solar photolysis experiments

Testing Date	Photolysis Test	Temperature (^oC)	Average Solar Intensity (W/m^2)	Duration of Clouds (min)	Photolysis Time (CST)
6/2/2015	DBPs photolysis kinetics	20 ± 2	1087	< 10	11:30 am – 5:30 pm
6/20/2015	Impact of pH on DBPs photolytic degradation	21 ± 1	1113	< 10	11:30 am – 5:30 pm
7/22/2015	Impact of nitrate/nitrite on DBPs photolytic degradation	22 ± 3	1102	< 10	11:30 am – 5:30 pm
8/2/2015	Impact of NOM on DBPs photolytic degradation	22 ± 2	1139	< 10	11:30 am – 5:30 pm

Table 4.2: TOX variations of DBPs in the dark

DBPs (C/C_0)	pH 6	pH 7	pH 8
DCAcAm	98 ± 2	98 ± 2	101 ± 2
CH	99 ± 1	98 ± 2	98 ± 1
Chloroform	98 ± 2	98 ± 2	98 ± 2
DCAN	96 ± 3	99 ± 1	97 ± 3
DBAN	98 ± 2	97 ± 2	97 ± 2
Bromoform	98 ± 2	97 ± 3	100 ± 2
TCNM	99 ± 1	101 ± 1	99 ± 1
MCAA	99 ± 1	96 ± 4	97 ± 3
MBAA	97 ± 3	97 ± 2	98 ± 2
DCAA	98 ± 2	97 ± 2	98 ± 2
DBAA	102 ± 2	98 ± 1	99 ± 1
TCAA	99 ± 1	98 ± 2	100 ± 1
MIAA	99 ± 1	98 ± 2	97 ± 2
TBAA	97 ± 2	100 ± 1	98 ± 1
DIAA	98 ± 1	96 ± 4	99 ± 1
TIAA	96 ± 3	97 ± 2	98 ± 2
Iodoform	97 ± 2	99 ± 3	98 ± 2

a. Each C/C_0 shows the average and standard deviation from the duplication experiments.
b. Experimental time = 30 min for DIAA, TIAA, and iodoform; and 6 h for others.

Table 4.3: First order rate constants for solar photolytic dehalogenation of DBPs

DBPs	k_p (h^{-1})	Half-life (h)	R^2
Trichloronitromethane (TCNM)	0.173 ± 0.007	4.0 ± 0.2	0.984
Bromoform	0.095 ± 0.003	7.1 ± 0.3	0.988
Dibromoacetonitrile (DBAN)	0.080 ± 0.002	8.7 ± 0.3	0.999
Tribromoacetic acid (TBAA)	0.046 ± 0.001	15.1 ± 0.5	0.976
Monoiodoacetic acid (MIAA)	0.036 ± 0.001	19.3 ± 0.8	0.983
DBPs	k_p (min^{-1})	Half-life (min)	R^2
Iodoform	0.132 ± 0.003	5.3 ± 0.2	0.998
Triiodoacetic acid (TIAA)	0.082 ± 0.004	8.5 ± 0.6	0.990
Diiodoacetic acid (DIAA)	0.068 ± 0.003	10.2 ± 0.6	0.991

a. Each first-order rate constant shows the average value and 95% confidence intervals from linear regression of the individual logarithmic kinetic points.

b. Each half-life shows the average value and the standard deviation calculated from the 95% confidence intervals of the rate constant.

Table 4.4: UV254 (cm^{-1}) of DBP solutions with spiked NOM before photolysis

NOM	DOC (mg/L)	MIAA	DBAN	Bromoform	TCNM	DIAA	TIAA	Iodoform
PLFA	0	0.015	0.021	0.028	0.035	0.061	0.067	0.081
	10	0.215	0.229	0.238	0.251	0.257	0.263	0.277
	20	0.521	0.533	0.541	0.552	0.564	0.571	0.582
SRHA	10	0.522	0.528	0.535	0.539	0.543	0.555	0.572
	20	0.943	0.957	0.961	0.966	0.971	0.988	1.055

a. Initial TOX concentration was 300 ± 10 μg/L as Cl, Br or I for chlorinated, brominated or iodinated DBPs.

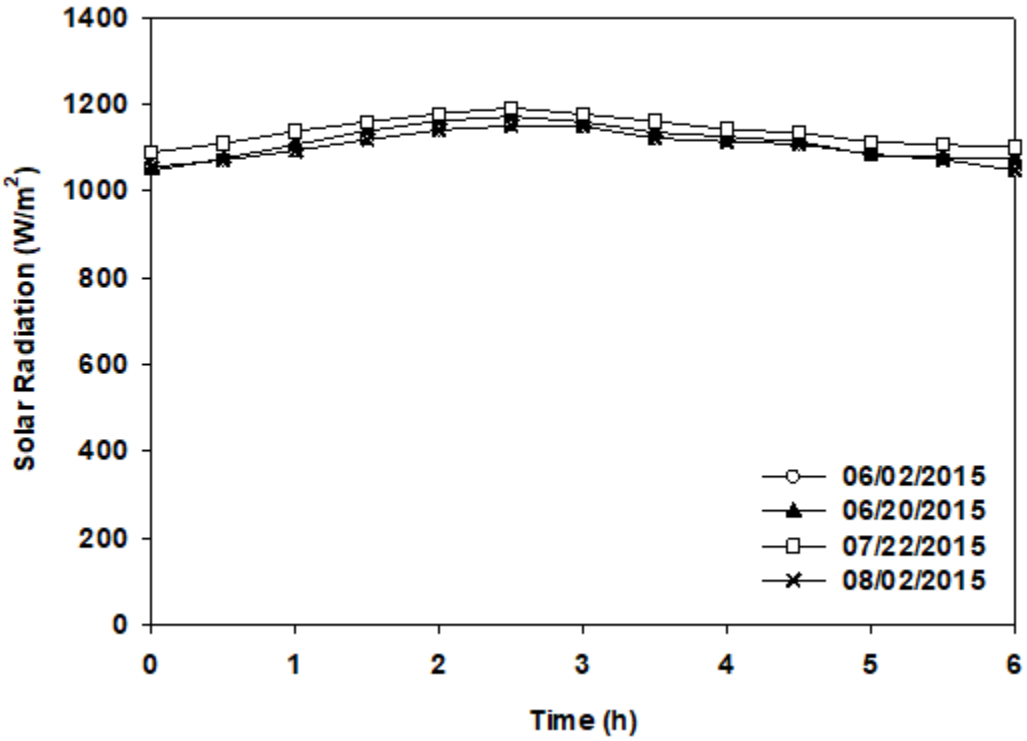

Figure 4.1: Solar radiation intensities for DBP photolysis experiments

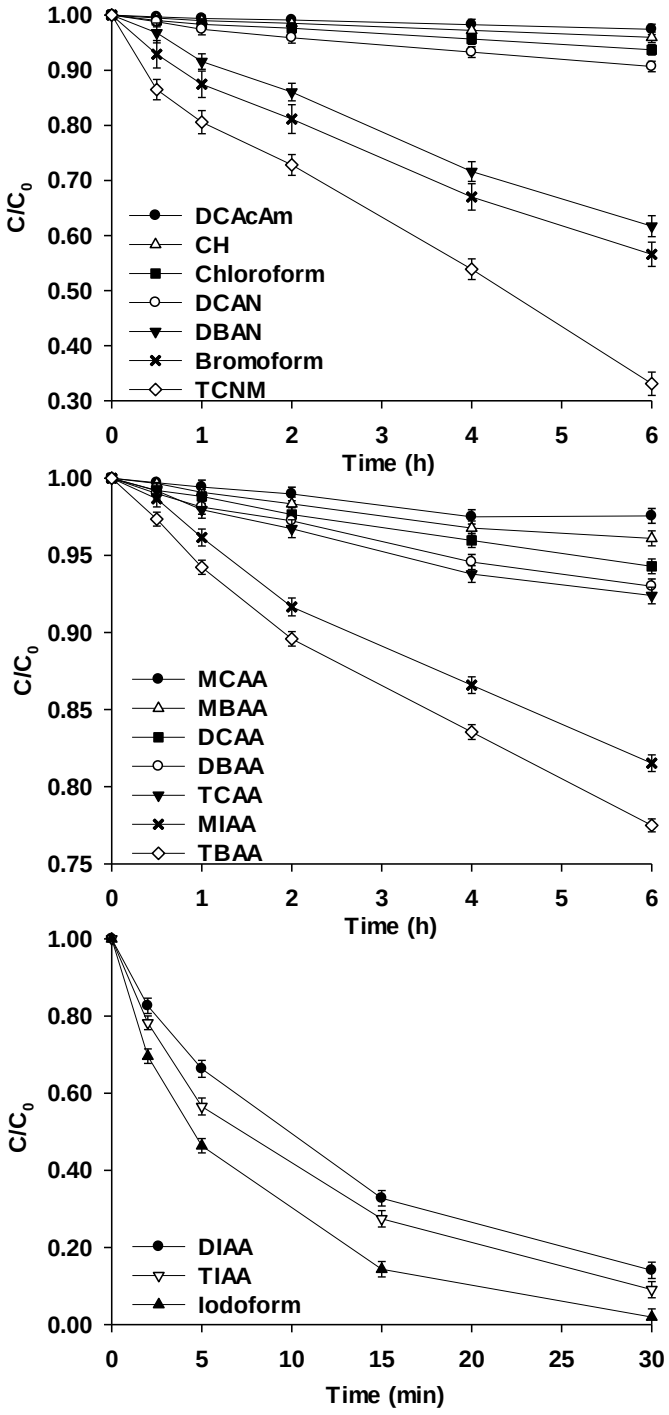

Figure 4.2: Effect of natural sunlight irradiation times on DBPs degradation

(Error bars show standard deviations obtained from duplicate experiments.)

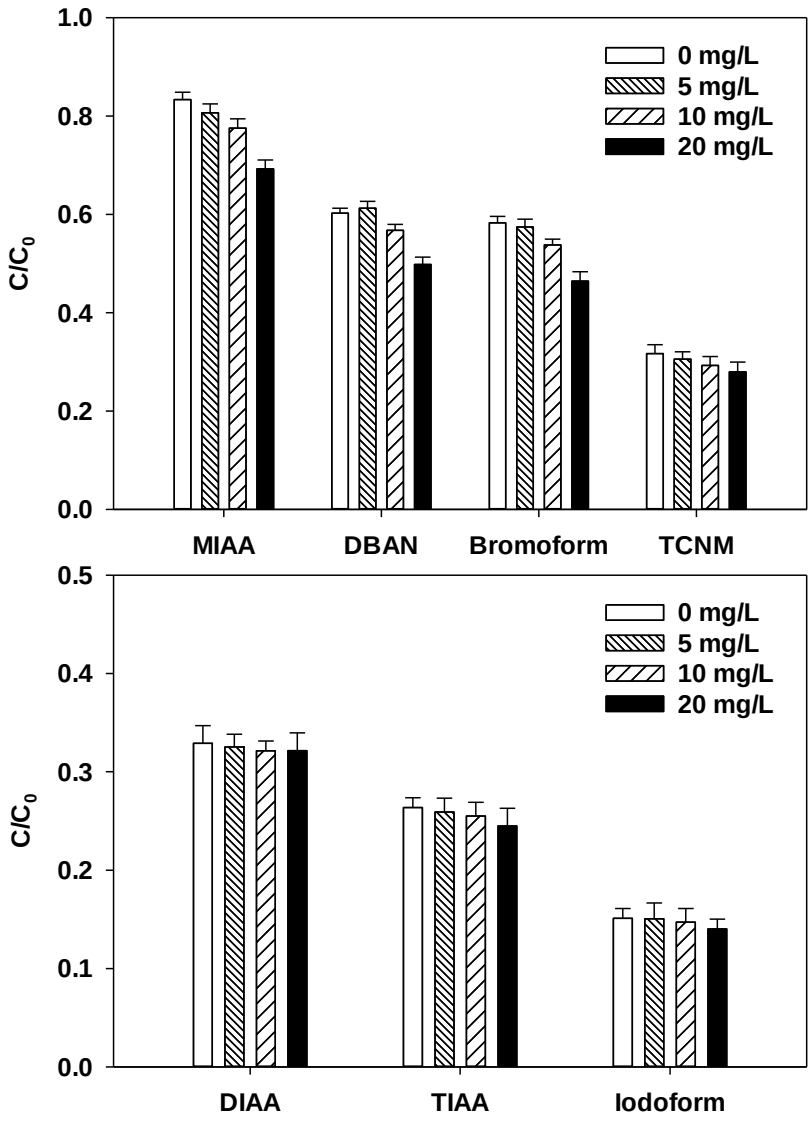

Figure 4.3: Effect of nitrate on photolytic dehalogenation of DBPs by natural sunlight

(Photolysis time=6 h for MIAA, DBAN, bromoform and TCNM and 15 min for DIAA, TIAA and iodoform; Error bars show standard deviations obtained from duplicate experiments.)

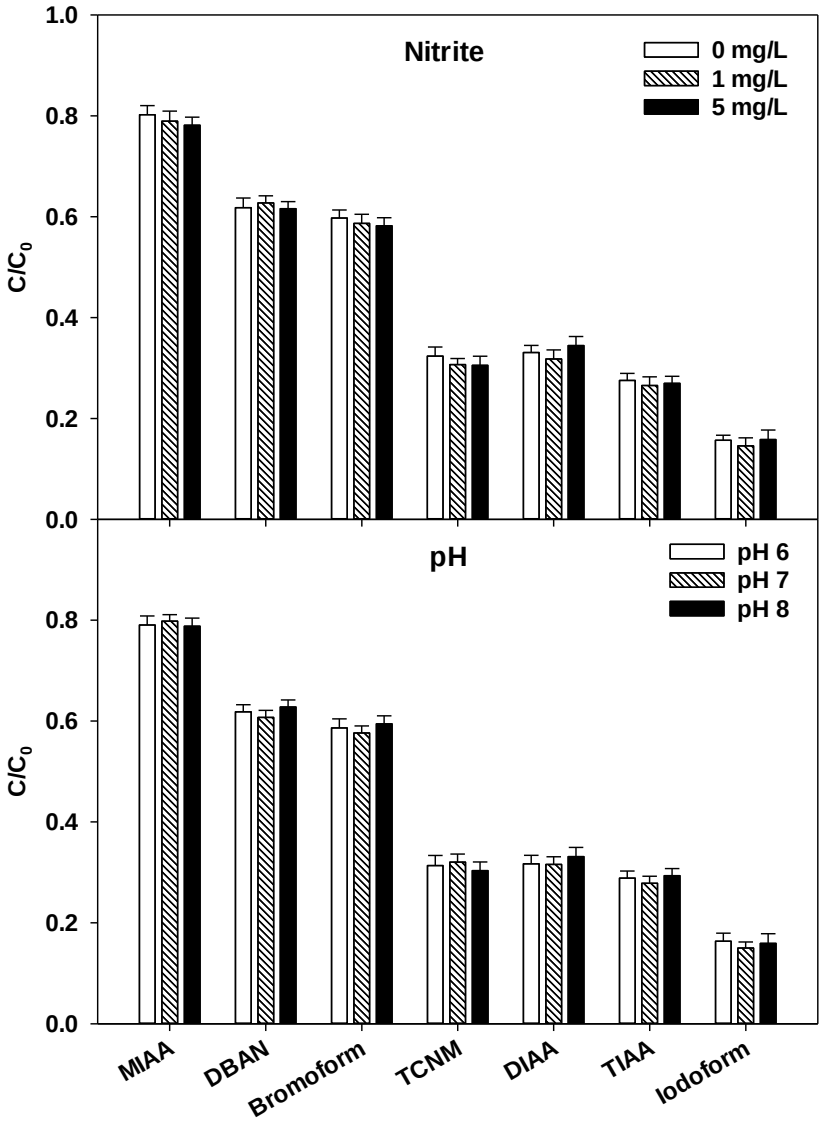

Figure 4.4: Effect of nitrite and pH on photolytic dehalogenation of DBPs by natural sunlight

(Photolysis time=6 h for MIAA, DBAN, bromoform and TCNM and 15 min for DIAA, TIAA and iodoform; Error bars show standard deviations obtained from duplicate experiments.)

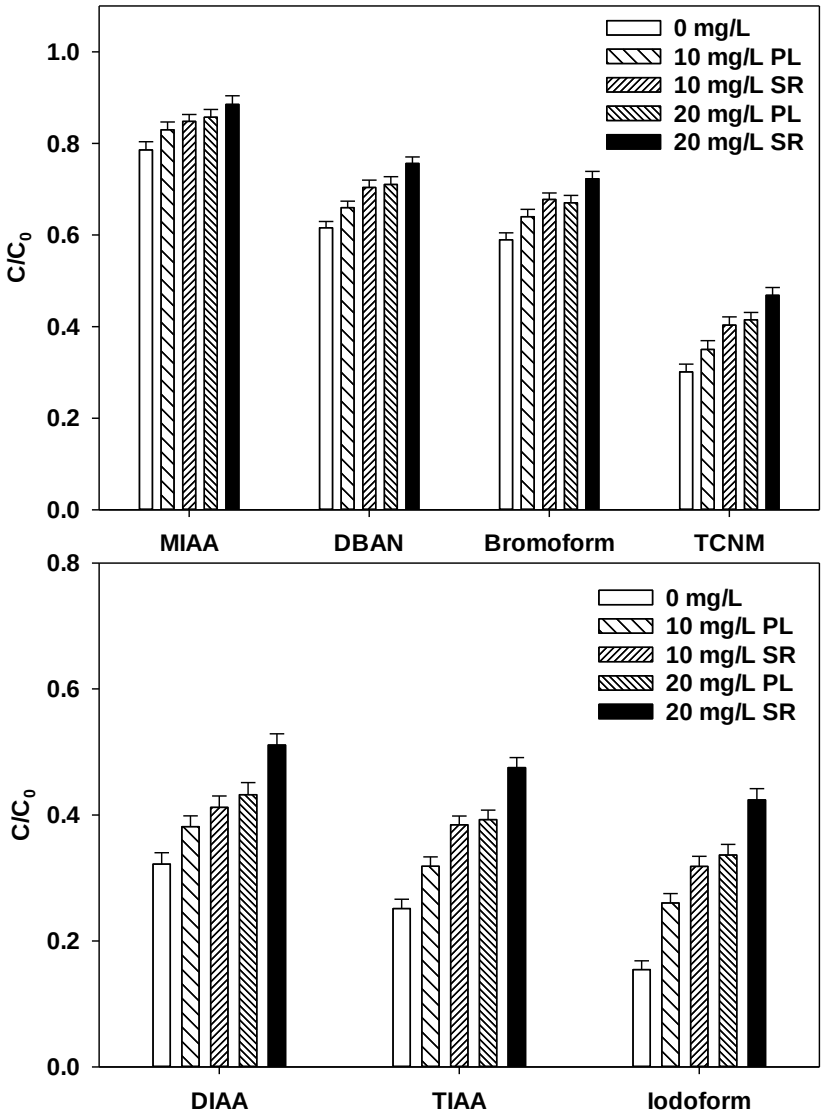

Figure 4.5: Effect of PLFA and SRHA on photolytic dehalogenation of DBPs by natural sunlight

(Photolysis time=6 h for MIAA, DBAN, bromoform and TCNM and 15 min for DIAA, TIAA and iodoform; Error bars show standard deviations obtained from duplicate experiments.)

CHAPTER FIVE
PHOTOCATALYTIC DEGRADATION OF DISINFECTION BYPRODUCTS USING NATURAL SUNLIGHT AND TIO_2

Abstract

The widespread of toxic disinfection byproducts (DBPs) in wastewater effluent and aquatic environment is raising the public concerns. Water reuse practices use wastewater effluents and surface water to augment drinking water supplies, therefore DBPs may present in drinking water causing serious health concerns. As a result, there is growing interest in the development of cost-effective and efficient process to remove DBPs and transform them to non-toxic safe byproducts. In this study, heterogenous natural solar photocatalysis process by titanium dioxide (TiO_2) has been investigated for the removal of total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI) in water. At 100 mg/L of (Aeroxide P25) TiO_2 and at pH 7.0, total organic halogen (TOX) photocatalytic degradation followed first order kinetics and the rates increased in the order of TOI > TOCl (NH_2Cl) > TOBr > TOCl (Cl_2), where the half-lives were 2.7, 5.0, 11.0 and 42.8 min, respectively. However, when the process applied in removing TOCl (Cl_2) and TOCl (NH_2Cl) in real water and wastewater samples, degradation rates decreased due to interferences by the presence of inorganic ions and dissolved organic carbon. For TOX species formed by fulvic acid, decreasing pH from 9 to 5 promoted TOX degradation rates by factor of 1.09-1.45. Moreover, the use of pure phases of TiO_2 anatase and rutile instead of mixed TiO_2 Aeroxide (80:20 anatase to rutile) have decreased TOX degradation rates significantly and the rate of inhibition increased in the order of rutile > anatase > 80:20 anatase to rutile. Hydrogen peroxide (H_2O_2) addition to

the process increased the photocatalytic degradation rate of TOCl (Cl_2) at concentration below 15 mg/L, due to increase in hydroxyl radical quantities, on the contrary, at higher H_2O_2 concentrations, the degradation declined due to hydroxyl radical scavenging and sunlight absorption by excessive H_2O_2. High molecular weight and hydrophobic TOCl (Cl_2) were more susceptible to solar photocatalytic process than corresponding low molecular weight and hydrophilic chlorinated compounds. Results demonstrate that solar-TiO_2 photocatalysis can be a very effective approach for degrading TOX species, particularly in low contaminated natural waters with neutral or acidic pH.

5.1 Introduction

Water scarcity has become a serious issue facing our communities due to the population growth, increased demands on water resources, and climate change. In the United States, water shortage has forced many cities to consider reusing municipal treated wastewater to augment drinking water supplies (Rodriguez et al. 2009). This has raised concerns about the potential impact of contaminants present in treated wastewater on drinking water quality (Snyder et al. 2003).

During disinfection practice at municipal wastewater treatment plants (MWTPs), disinfectants such as chlorine or chloramine are added to wastewater effluent prior to discharge, to deactivate microorganisms thus preventing the spread of waterborne diseases. However, disinfectants can also react with the naturally existing organic materials in water forming a suite of harmful disinfection byproducts (DBPs) including trihalomethanes (THMs), haloacetic acids (HAAs), trihaloacetaldehydes (THAs), haloacetonitriles (HANs), halonitromethanes (HNMs), haloacetamides, nitrosamines, and others (Hua and Reckhow 2008a, Krasner et al. 2009, Mitch and Sedlak 2002, Yang et al. 2005). Moreover, wastewater effluents typically have high levels of iodide and bromide concentrations from industrial discharges, which leads to the formation of iodinated and brominated-DBPs (Duirk et al. 2011, Krasner et al. 2009, Parker et al. 2014). Taxological studies have shown that continuous exposure of DBPs can cause carcinogenic and developmental effects that pose a serious health risks to public life (Plewa et al. 2004, Richardson et al. 2007). Thus, the United States Environmental Protection Agency have regulated four THMs and five HAAs in drinking water in an effort to reduce the health

risks associated with DBPs. Therefore, wastewater-derived DBPs may affect the quality of the source water for drinking water supplies.

Total organic halogen (TOX) is a collective parameter that has been used to measure the total concentration of halogenated DBPs in water. The analysis showed that THMs, HAAs and other identified DBPs only contribute to roughly 50% of TOX formed by chlorine, and 20% of TOX formed by chloramine (Hua and Reckhow 2008a, Zhang et al. 2000). The unknown fraction of TOX (UTOX) may contain substantial concentrations of potentially toxic DBPs that may explain the observed health risks associated with drinking water DBPs (Bull et al. 2001, Richardson et al. 2007). Therefore, it's very important to remove the unregulated and unidentified groups of DBPs from wastewater effluents to protect the public and the aquatic ecosystem.

DBPs have been observed to be persistent against conventional drinking water treatment processes (Gopal et al. 2007). Thus, wastewater-derived DBPs may end up existing in finished drinking water. Due to the increase in using water reuse programs, the concentration of wastewater-derived DBPs are expected to increase in the future, therefore this problem must be emphasized through wastewater treatment protocols, including the use of new technologies to completely remove DBPs prior to wastewater discharge into drinking water resources.

Natural solar photolysis is one of the natural biogeochemical processes that occur in surface water that may lead to decrease DBPs concentrations (Chen et al. 2008). Previous studies reported iodinated and brominated DBPs are more susceptible to sunlight than chlorinated DBPs (Abusallout and Hua 2016b, Chen et al. 2010). Additionally, the authors investigated TOX and individual DBPs degradation under

natural sunlight and half-life varied between 2.6 to 10.7 hr for TOX species, and 5.3 min to several days for individual DBPs (Abusallout and Hua 2016a, b). This relatively high half-lives indicated that solar photolysis cannot be used for water and wastewater treatment applications solely and can be only considered in combinations with other processes such as advanced oxidation processes (AOPs) to achieve complete removal of DBPs in very short period of time.

Among the different AOPs, natural solar heterogenous photocatalysis of metal oxide semiconductor such as titanium dioxide (TiO_2) in suspension has emerged as promising efficient process for the treatment of different organic pollutants in wastewater (Malato et al. 2002). Semiconductor particles such as TiO_2 can be excited through the most energetic part of solar spectrum ($\lambda < 400$ nm) leading to the generation excited-state electron and hole pairs (e^-/h^+) on the TiO_2 surface. Those pairs remove organic contaminates through redox reactions at the surface of TiO_2 and/or by hydroxyl radical ($^{\bullet}OH$) oxidation that generated by reaction of water molecules with the pairs (Gaya and Abdullah 2008, Pelaez et al. 2012). The main advantages of using TiO_2 as semiconductor that its cost-effective, non-toxic, eco-friendly, operate at wide pH range and can be activated by natural sunlight.

The present work is focused on the degradation of total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI) in water using heterogenous TiO_2 photocatalytic process under natural sunlight irradiation. Additionally, the research investigated the effect of different variables including pH, TiO_2 phase identity, common water oxidants and natural water contaminates on the TOX degradation rate. The results of this study

help determine the applicability of solar-TiO_2 photocatalytic process for reducing the health risks associated with toxic DBPs during water reuse.

5.2 Methods and Materials

5.2.1 Preparation of TOX Samples

In this experiment, TOX samples were prepared by dosing chlorine (3.0 mg/L as Cl_2), monochloramine (0.4 mg/L as Cl_2), bromine (2.0 mg/L as Br_2) and iodine (1.0 mg/L I_2) into Suwannee River Fulvic Acid (SRFA) solutions that have carbon concentration of 3.0 mg/L, to produce TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI, respectively. SRFA obtained from International Humic Substance Society and a widely used model humic organic matter for drinking water studies. Furthermore, two water and wastewater samples were collected after filtration process from Brookings water treatment plant (WTP) and Brookings MWTP, SD. The two samples were treated as received to produce TOCl (Cl_2) and TOCl (NH_2Cl) by adding 8.5 and 2.5 mg/L for the wastewater sample and 2.5 and 0.35 mg/L as Cl_2 for the drinking water sample, of chlorine and monochloramine, respectively. All TOX samples were treated in 300 ml demand free bottles and pH was adjusted to 7.0 ± 0.1 using NaOH or H_2SO_4 before placing the bottles in 20 °C incubator for 72 h. These specific conditions were selected to make sure all oxidant residuals were consumed at the end of 72 h. Chlorine, bromine and iodine stocks were prepared by diluting sodium hypochlorite solution (Fisher Scientific 4-6%), bromine solution (>99.5%, Sigma Aldrich) and solid iodine (>99.8%, Sigma Aldrich) in nanopure water, respectively. On the other hand, monochloramine stock was prepared freshly on-site 24 h before the experiment following a method previously published (Abusallout and Hua 2016a). The resulting TOX concentrations before solar

photocatalytic experiments were 451 ± 15 µg Cl/L, 47 ± 5 µg Cl/L, 272 ± 12 µg Br/L and 155 ± 8 µg I/L for TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI, respectively.

5.2.2 TOX Hydrophobicity and Molecular Weight Determination

The hydrophobic and molecular weight (MW) fractionation experiment was only conducted on TOCl (Cl_2) formed by SRFA. To determine the hydrophobic fractions, TOCl (Cl_2) sample was acidified to pH 2.0 using sulfuric acid and then passed through DAX-8 resin (Sigma Aldrich, St Luis, MO) to absorb the hydrophobic fraction. Effluent from DAX-8 was referred to as hydrophilic fraction. To extract the hydrophobic TOCl (Cl_2) fraction from DAX-8 resin, a solution of 0.1 N NaOH was separately passed through the resin in reverse direction. After extraction, pH was immediately adjusted to 7.0 and the volume was adjusted back to the initial sample volume.

To determine the MW fractions, each TOCl (Cl_2) sample was fractionated by membrane filter with cutoff of 1 kDa (EMD Millipore PLAC ultrafiltration membrane Billerica, MA) into two fractions; low MW (< 1 kDa) and high MW (> 1 kDa). The filtration was performed using stirred 400 mL Amicon ultrafiltration cell. Starting of volume of 400 ml of TOCl (Cl_2), sample was filtered until the retentate volume decreased to 75 ml, then the filtration stopped and the permeate collected was referred to as low MW TOCl (Cl_2) (< 1 kDa). To remove any MW compounds lower than the membrane cutoff from the 75 mL retentate, deionized water was added to bring back the volume to 400 mL and the filtration process started again until 75 mL retentate achieved. This step was repeated at least three times to make sure only MW higher than 1 kDa cutoff was left in the 75 mL retentate, then it was referred to as high MW TOCl (Cl_2) (> 1 kDa).

5.2.3 Natural Solar Photocatalytic Experiments

TiO_2 solar photocatalytic experiments were conducted outdoors, under natural sunlight using 60 mL quartz tubes (25 mm outside diameter, 150 mm length and 1.5 mm wall thickness). The tubes were capped tightly (to reduce volatilization) and placed on inclined platform at 30° angle in an open place next to the Water and Environmental Engineering Research Center (44°18'53.5"N, 96°47'09.7"W) at Brookings, SD. The experiments were performed between May and September of 2016 on selected sunny days starting at 11:30 am to 3:30 pm. During the experiments, natural sunlight intensity was monitored using a photometer (Seaward 396A916, Tampa, FL) every 15 min and it averaged 1154 ± 68 W/m^2. Temperature was recorded to be 27 ± 2 °C. The clouds were also observed during the experiments, and the irradiation time was extended to meet the 4 h solar exposure, if needed.

In this study, TiO_2 used was nanophase Aeroxide (P25) obtained from Sigma Aldrich. It is a mixture of anatase and rutile phases with weight ratio of 80/20, specific surface area of 50 m^2/gm and an average particle diameter of 21 nm . TiO_2 aqueous stock solutions were prepared at least 24 h prior to the start of the experiments, to ensure a complete hydration of TiO_2 surface. TOX samples and TiO_2 were mixed at pH 7.0 for 30 min in darkness prior to solar exposure to ensure stabilization and equilibrium for the mix. Samples were also measured for dissolved oxygen and assured to be in phase of saturation (> 8.0 mg O_2/L). Afterwards, samples were exposed to natural sunlight for maximum of 4 h and the pH was controlled during the experiments using NaOH and H_2SO_4. Chemical buffers were avoided in this study, since they might interfere with the photocatalytic process**.** TiO_2 was kept in suspension during the experiments by inverting

samples carefully every 2-3 min. Stirring was avoided since it increases volatilization effects of DBPs. After the required solar exposure time for each TOX sample, TiO_2 was separated from the aqueous solution by centrifuge, and the pH for supernatant was dropped to 2.0 using concentrated nitric acid and then stored in 4 °C for further TOX analysis.

Total of six experiments were conducted to evaluate the performance and applicability of TiO_2 natural solar photocatalytic process for removal of TOX in water. Tests included impact of TiO_2 loading, time, pH, TiO_2 phase identities, hydrogen peroxide (H_2O_2) and MW and hydrophobicity. The goal of the first test was to determine the optimal TiO_2 dose that will be used for the further experiments based on the highest TOX removal and lower TiO_2 loading as possible. TiO_2 concentrations were selected as follow 25, 50, 100, 200 and 400 mg/L. Additionally, the test determined the extents of TOX adsorption on TiO_2 surfaces in darkness, where a duplicate batch of TOX samples covered with aluminum foil was placed next to the other TOX tubes that were exposed to natural sunlight outdoors. The second experiment investigated the impact of pH variations 5 to 9 on TOX degradation by the TiO_2 photocatalytic process. The third experiment compared the using of commercially available pure TiO_2 phases included pure anatase (Hombikat UV-100, 186 m^2/gm) and rutile (TiOxide, 3.5 m^2/gm) to the mixed Aeroxide P25 (80:20 anatase to rutile) for the removal of TOX species. The fourth experiment examined the effect of common oxidants used in WTPs for disinfection purposes including H_2O_2, on the efficiency of TiO_2 solar photocatalytic process for TOX removal. H_2O_2 concentrations used were 2, 6, 15, 30 and 60 mg/L. The fifth experiment determined the extents of TOX degradation in regard to their MW and hydrophobicity

fractions using TiO_2 natural solar photocatalytic process. The sixth experiment investigated real water and wastewater TOX degradation via TiO_2 solar photocatalytic process, to determine the effectiveness of the process under the presence of different natural water contaminants as function of time.

5.2.4 Analytical Procedures

Chlorine, chloramine, bromine and iodine concentrations were determined using DPD ferrous titrimetric method. DOC concentrations were measured using TOC analyzer-5000 by Shimadzu following Standard Method 5310 B. Chloride, bromide, iodide, nitrate and sulfate ion levels were measured using ion chromatography (DX-500) equipped with conductivity detector (CD-20) from Dionex. TOX concentrations were analyzed by TOX-100 analyzer (Cosa Xentaur Inc., Norwood, NJ) that uses an adsorption-pyrolysis-titration method following a standard method 5320 B with minor modification. Pure chlorine, bromine and iodine were used for SRFA solutions, and since SRFA does not contain traces of bromide or iodide ions, TOX was expressed as halogen-specific TOX. TOX recovery tests were conducted using individual DBPs and averaged between 95 to 105%, which were very similar to previous experiment. DBPs tested included bromoform, iodoform, dichloroacetonitrile, monoiodoacetic acid, dichloroacetic acid, dibromoacetic acid, and trichloroacetic acid. TiO_2 separation from the aqueous solutions were conducted using a centrifuge for 30 min at 4 °C and speed of 15,000 rpm (Sorvall ST 8R, ThermoFisher Scientific, Germany).

5.3 Results and Discussion

5.3.1 Kinetics of TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI Solar Photocatalytic Decomposition

The adsorption of TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI species by TiO_2 particles were tested in dark for 4 h. When the highest loading of catalyst was used (400 mg/L), the results showed less than 10% of TOX was adsorbed. Therefore, TiO_2 loading doses for the experiments that conducted in the presence of natural sunlight were varied between 25 and 400 mg/L. Table 5.1 presents the initial degradation rates (r_0) of TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI by different TiO_2 loadings in the presence of natural sunlight. The results showed all the four TOX species exhibited similar trend, where r_0 values were increased by increasing TiO_2 amount until 100 mg/L then slightly dropped when 200 and 400 mg/L were in use, indicating decrease in the photodegradation efficiency at higher TiO_2 concentrations. The initial observed increase in photodegradation between 25 and 100 mg/L of TiO_2, can be explained in terms of increase in availability of active sites at TiO_2 that subsequently can be activated by sunlight leading to increase the photocatalytic degradation kinetics of TOX (Hu et al. 2007). However, higher loads of catalyst can also prevent the transmission of the natural sunlight into the suspension, therefore, reducing the amount of solar activated TiO_2 surfaces that reduce the photocatalytic degradation (Michael et al. 2010). Additionally, agglomeration can take place due the high availability of TiO_2 particles that interact, resulting in lower surface area to absorb sunlight (Evgenidou et al. 2007). From Table 5.1, its apparent that the optimum concentration of TiO_2 needed to increase the TOX photodegradation rates to the highest is at 100 mg/L.

Fig 5.1 demonstrate the photocatalytic degradation of TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI using 100 mg/L TiO_2 at pH 7.0 under natural sunlight. TOBr, TOCl (NH_2Cl) and TOI have exhibited complete dehalogenation in 60, 30 and 20 min of natural sunlight exposure, where TOCl (Cl_2) was the most resistant with 70.3% removal after 60 min. Table 5.1 presents the apparent first order rate constants and linear regression coefficients (R^2) for the four TOX species at different concentrations of TiO_2 in the presence of natural sunlight. The photocatalytic degradation followed first order kinetics as evidenced by the relatively high R^2 (> 0.90). At 100 mg/L TiO_2, the half-lives for the TOX species were calculated to be 42.8, 11.0, 5.0 and 2.7 min for TOCl (Cl_2), TOBr, TOCl (NH_2Cl), and TOI.

To ensure TOX degradation was only caused by the photocatalytic process, control TOX samples without TiO_2 were exposed to natural sunlight. Results showed TOX degradation less than 10% by solar photolysis which are consist with the authors previous published results (Abusallout and Hua 2016a).

In terms of driving force, photoexcitation of TiO_2 generates highly oxidative ($E° = +2.7$ V) valance band holes (h_{vb}) and moderately reductive ($E° = -0.5$ V) conduction band electrons (e_{cb}). Those h_{vb}/e_{cb} pairs are capable of degrading organic compounds via trapping by h_{vb}, reactive oxygen species ($^{\bullet}OH$, $^{-}O_2^{\bullet}$, $^{\bullet}HO_2$) and/or reduction by e_{cb} (Gaya and Abdullah 2008). Since TOX had been observed to have insignificant adsorption on TiO_2 surface, trapping by h_{vb} degradation mechanism had been neglected. The next section discusses the effect of reactive oxygen species and conduction band electron holes on TOX photocatalytic degradation.

The formation of strongly oxidative •OH is the most common degradation mechanism reported by literature for TiO_2 solar photocatalytic process. It results of reaction by h_{vb} and an adsorbed water molecule that act as an electron donor. However, due to the lack of oxidizable functional groups such as carbon-hydrogen and unsaturated bonds, •OH radicals hardly react with halogenated organic compounds. By contrast, previous studies reported THMs and HAAs including chloroform ($CHCl_3$), bromoform ($CHBr_3$) and dichloroacetic acid ($CHCl_2COOH$) had to completely dehalogenase to their conjugate acid and carbon dioxide after applying TiO_2 photocatalysis process (Bahnemann et al. 2002, Choi and Hoffmann 1996, Gan et al. 2018, Kormann et al. 1991, Ollis et al. 1984, Rodríguez et al. 2005, Zalazar et al. 2008). Those DBPs undergo initial hydrogen abstraction leading to the formation of unstable halogenated compounds such as phosgene that can be quickly hydrolyzed to release their substituted halogens in water. This also agrees with newly generated prediction model of DBPs degradation by •OH radical, that proves that •OH radicals are capable of removing aliphatic halogenated DBPs through indirect oxidation initiated by •OH radical (Chuang et al. 2016b). Additionally, in another study by the authors (not published yet), individual DBPs and TOX species had been examined under modified solar fenton process that utilize •OH radicals as the only degradation mechanism. As expected, individual aliphatic DBPs exhibited different degradation extents, and the rates were increased based on the type of carbon-halogen bond (I > Br > Cl), increase in number of carbon-hydrogen bonds and the type of functional side group associated with DBPs. On the other hand, TOCl (Cl_2), TOBr and TOCl (NH_2Cl) were susceptible to the process and degraded up to 67.4, 75.9 and 90.1% after 60 min of operation, respectively. This is clearly demonstrated that in

addition to the aliphatic DBPs, the unknown fraction of TOX (UTOX) which may contain double bonds and aromatic halogenated DBPs can be susceptible to $^{\bullet}OH$ radical oxidation mechanism via $^{\bullet}OH$ radical addition and hydroxide ion nucleophilic substitution at neutral pH (Augugliaro et al. 2012, Liu et al. 2018). However, solar fenton process was not efficient enough to entirely dehalogenase TOX species particularly for TOCl (Cl_2) and TOBr. Comparing to the current study, TiO_2 solar photocatalysis process was considerably better in eliminating all four TOX species. This may due to the involvement of reduction process by the photoexcited e_{cb} at the surface of TiO_2 nanoparticles.

e_{cb} primary reacts with dissolved oxygen available in the aqueous solution that serve as scavenger and electron accepter, leading to the formation of oxygen radicals ($^{-}O_2^{\bullet}$, $^{\bullet}HO_2$). However, e_{cb} also can directly transfer to the halogenated compounds inducing their reductive degradation or transformation. CCl_4 and other halogenated organic compounds had been observed to undergo some reductive dehalogenation by UV-TiO_2 generated e_{cb} in the presence of different levels of dissolved oxygen (Bahnemann et al. 1987, Choi and Hoffmann 1995, 1996). However, under normal conditions the redox potential of e_{cb} is not significantly negative enough to be strong reducing agent. Consequently, it's expected that during TOX photocatalytic degradation, both oxidative and reductive pathways were operating, and this have been reported in literature for the degradation of chlorinated compounds (Choi and Hoffmann 1996, Zalazar et al. 2005). Therefore, to determine if this assumption is correct, the reductive pathway can be entirely terminated by scavenging the photogenerated e_{cb} using better electron acceptor (other than oxygen) such as hydrogen peroxide (H_2O_2) forming instead

•OH radical (Jedsukontorn et al. 2016). Fig 5.2 demonstrate the effect of 2 to 60 mg/L of H_2O_2 on the TOCl (Cl_2) after 60 min of solar TiO_2 photocatalytic process. The results showed that increase in H_2O_2 concentration causes an increase in degradation rate of TOCl (Cl_2) by 4.5 and 12.8% for 6 and 15 mg/L of H_2O_2, respectively. However, at higher concentrations, the solar TiO_2 photocatalytic process was inhibited and decreased TOCl (Cl_2) degradation by 2 and 9.6% for 30 and 60 mg/L of H_2O_2, respectively. The observed increase in TOCl (Cl_2) at lower doses of H_2O_2 is due to the increase in •OH radical formation. It has been reported that the addition of H_2O_2 in mixed anatase and rutile TiO_2 increased •OH radical formation by 10-20% (Hirakawa et al. 2007). In contrary, the presence of excess H_2O_2 scavenges the photogenerated oxidizing species including •OH radicals, wasting them to oxygen and protons (Kritikos et al. 2007). Additionally, H_2O_2 can be absorbed on TiO_2 surface, thus decreasing it surface catalytic and sensitive activity to sunlight (Konstantinou and Albanis 2004). Another adverse effect of excess H_2O_2 is that it reacts with TiO_2 forming peroxo compounds that terminate the photocatalytic efficiency of TiO_2 (Poulios et al. 2000). Therefore, to enhance TOX photocatalytic degradation by TiO_2 to the maximum, the need of optimal concentration of H_2O_2 is essential. The results from this experiment clearly demonstrate that oxidation by •OH radicals is the dominant mechanism for TOX degradation by solar TiO_2 photocatalytic process, regardless of the involvement of the reductive e_{cb}.

To further analyze TOX solar photocatalytic degradation by TiO_2, TOCl (Cl_2) was fractionated based on molecular weight and hydrophobicity to four different fractions: MW > 1 kDa, MW < 1 kDa, hydrophobic (HPO) and hydrophilic (HPI). Afterwards, those fractions were exposed separately to the solar photocatalytic process at 100 mg/L

TiO_2 at pH 7.0 for 1 h, and the results are presented in Fig 5.3. Before applying the photocatalytic treatment, TOCl (Cl_2) consisted of 51.8 and 48.2% of MW < 1 kDa and MW > 1 kDa fractions, respectively. However, the results showed that after applying solar-TiO_2 photocatalytic process, final MW fractions percentage were 22.9 and 8.8%, respectively. Similarly, TOCl (Cl_2) HPO and HPI fractions comprise about 49.4 and 50.6% in control samples. However, solar-TiO_2 photocatalytic process decreased their concentrations to 5.4 and 26.3%, respectively. It's clear that the photocatalytic process was better in eliminating MW > 1 kDa and HPO fractions by 39.4 and 44%, respectively, where it was less effective for MW < 1 kDa and HPI fractions with 28.9 and 24.3% removal, respectively.

Its known that MW < 1 kDa and HPI fractions contain the known low MW aliphatic chlorinated DBPs which comprise about 50% of total TOCl (Cl_2) including THMs, HAAs, HANs, HNMs and others. Those DBPs are recognized for their higher stability against $^{\bullet}OH$ radical attacks, therefore the lower degradation observed was expected. On the contrary, the MW > 1 kDa and HPO fractions comprise the other 50% of total TOCl (Cl_2) that contains the unidentified group of chlorinated DBPs. New studies reported that those DBPs are expected to contain high UV absorbance aromatic rings and double compounds (Zhang and Minear 2002) such as new identified halophenolic DBPs (Xiao et al. 2012), that are well recognized to be susceptible by $^{\bullet}OH$ radical oxidation (Augugliaro et al. 2012). Therefore, the higher degradation observed for MW > 1 kDa and HPO fractions by $^{\bullet}OH$ radicals agrees with those findings.

In conclusion, natural solar photocatalytic process by low TiO_2 dose and at neutral pH is very effective process for the removal of the four TOX species, and the

order of degradation increased as follow: TOI > TOCl (NH_2Cl) > TOBr > TOCl (Cl_2). To our knowledge, this is the first study in literature that investigated and successfully degraded TOX species in water by this process.

5.3.2 Effect of Varying pH on TOX Solar Photocatalytic Degradation by TiO_2

The solar photocatalytic degradation by 100 mg/L TiO_2 of TOCl (Cl_2), TOBr, TOCl (NH_2Cl) and TOI have been investigated at various pH values (pH 5, 7 and 9) and the apparent first order kinetics are given in Fig 5.4. Varying pH in TOX control samples at dark and under natural solar photolysis process only, did not have significant effect on TOX initial concentrations. Although, the authors at previous research reported increase of all TOX degradation at higher pH values after 6-hr of solar photolysis (Abusallout and Hua 2016a), this affect is neglected since solar exposure time is significantly lower in this experiment.

The results in Fig 5.4 show enhance in degradation kinetics of TOCl (Cl_2), TOBr, TOCl (NH_2Cl) and TOI by 19, 27, 37 and 45 percentage points, respectively, when pH decreased from 9 to 5. It's clearly that TOX photocatalytic degradation by TiO_2 favors acidic conditions rather than alkaline. In literature, degradation rate of targeted organic compounds may vary with pH due to change of TiO_2 surface properties, rate of reactive oxygen radical formation and ionization state of organic compounds (Abellán et al. 2007). TiO_2 (Aeroxide P25) surface is at neutral charge (Point of zero charge-pzc) at pH 6.25 (TiOH) (Chou and Liao 2005). Therefore, at pH < 6.25 TiO_2 surface is positively charged ($TiOH_2^+$) and at pH > 6.25 is negatively charged (TiO^-). It's expected that at pH 5.0 the acidic DBPs in the four TOX species including HAAs (pKa < 3) can server as

electron donor and react extensively with the positively charged TiO_2 surface specifically by h_{vb}^+, since HAAs are negatively charged. Studies reported higher degradation of HAAs at pH lower than 6.0 including trichloroacetic acid and dichloroacetic acid by suspended TiO_2 photocatalytic process (Bahnemann et al. 2002, Kormann et al. 1991). This can explain the observed increase in TOX photocatalytic degradation in this study since HAAs group comprise about 25% of total TOX. Additionally, the unregulated and unidentified group of DBPs may contain species with lower pKa values and behave like HAAs and thus induce total TOX degradation by solar TiO_2 process at acidic pH. On the contrary, at alkaline pH 9, TOX photocatalytic removal was inhibited and that could be attributed to electrostatic repulsion by the negatively charged at TiO_2 particles, that prevent neutral and negative charge DBPs including THMs and HAAs, respectively to be adsorbed at TiO_2 surface at alkaline pH. Studies reported lower to no degradation of chloroform and trichloroacetic acid at alkaline pH by TiO_2 photocatalytic process (Kormann et al. 1991). Furthermore, at alkaline pH values, generated $^{\bullet}OH$ radicals are rapidly scavenged, and they will not be able to react with organic compounds (Michael et al. 2010), thus dissuade total TOX degradation.

5.3.3 Effect of TiO_2 Phase Identity on TOX Photocatalytic Degradation

Fig 5.5 shows the results of an experiment to characterize the effect of different commercially available TiO_2 phases on TOX photocatalytic degradation including Hombikat UV-100 and TiOxide. The experiment was conducted on mass loading normalized basis at 100 mg/L of TiO_2 and pH 7.0 under maximum of 1-hr of natural sunlight. The results show that, all TOX species were much faster in degradation by the mixed anatase/rutile TiO_2 (Aeroxide) in comparison to the other two pure phases of TiO_2

rutile (TiOxide) and TiO_2 anatase (Hombikat UV-100). The observed reactivity followed the order of Aeroxide >> Hombikat UV-100 > TiOxide. The most inhibition observed when pure rutile was in use and TOX degradation observed was between 6.2 to 20.7% for the four species. However, when pure anatase was in use, degradation was clearly better than rutile with observed degradation between 19.3 and 62.8%. This observed difference in degradation between the two phases is attributed to the structure characteristics of each TiO_2, where anatase has 53 more surface area, stronger sunlight absorption (specifically visible wavelength) and smaller particle size than rutile (Haque et al. 2017). Thus, creating more h_{vb}/e_{cb} pairs that leads to more $^{\bullet}OH$ radicals formation. On the other hand, the use of the mixed anatase/rutile TiO_2 led to the highest degradation of TOX species between 69.3 to 99%. Many studies have reported the benefits of using the mixed anatase/rutile TiO_2 for removal of different contaminants in water. Reports suggest that the mix phase combine the advantages of both TiO_2 phases, where it easier to separate h_{vb}/e_{cb} pairs from anatase phase to rutile phase, thus extending their lifetime (Jiang et al. 2007).

5.3.4 Effect of Real Water and Wastewater Matrix on TOX Photocatalytic Degradation by TiO_2

Table 5.2 presents water quality characteristics of Brookings water and wastewater filter samples collected freshly 24 h before experiment. Due to the higher DOC concentration in MWTP sample comparing to WTP sample, TOX formation was significantly higher after both chlorination and chloramination. Additionally, both real water samples contain some bromide that might be oxidized forming brominated DBPs, however, it's expected that chlorinated and chloraminated DBPs are the predominant, since the measured bromide levels are very low.

Fig 5.6 shows the first-order solar-TiO_2 photocatalytic kinetics of TOX compounds formed by WTP and MWTP water samples. Results showed that TOX degraded faster in drinking water than wastewater sample. TOCl (Cl_2) and TOCl (NH_2Cl) in drinking water showed increase in degradation rate constants by 92% and 115%, respectively than in wastewater. The observed degradation differences can be mainly attributed to the combined effects and different concentrations of DOC and alkalinity between both waters. For the wastewater TOX, DOC concentration is very high (Table 5.2) in comparison with drinking water and therefore it competes with TiO_2 over sunlight absorption (Minero et al. 1999). Moreover, presence of high concentration of bicarbonate and carbonate in wastewater can scavenge generated $^{\bullet}OH$ radicals forming weaker oxidation agent ($CO_3^{\bullet -}$), that is several orders slower in reactions with organic compounds than $^{\bullet}OH$ radicals (Bhatkhande et al. 2002). However, due to relatively low concentrations of DOC and alkalinity in drinking water (Table 5.2), their impacts were limited in comparison to wastewater TOX. Therefore, typical drinking water characteristics should be ideal for solar TiO_2 photocatalytic applications.

It's important to mention that inorganic ions present in real water including chloride, sulfate, nitrate and bromide have been reported to decrease TiO_2 photocatalytic process by competing severely over adsorption sites on TiO_2 particles, therefore reducing the overall organics adsorption (Chen et al. 1997). However, since TOX compounds have low adsorption capabilities on TiO_2 and inorganic ions do not absorb excitation light, thus their impact has been neglected.

5.4 Conclusions

Treated municipal wastewater effluent contain a substantial amount of toxic wastewater derived-DBPs that may cause health issues for the public and aquatic life. AOPs including heterogenous TiO_2 photocatalysis process have been widely implemented for removal of toxic persistent organic compounds through oxidation by hydroxyl radical. This study was conducted to investigate the effect of natural solar-TiO_2 photocatalytic process on the removal of TOX compounds in water at neutral pH. TOX photocatalytic degradation by 100 mg/L of (Aeroxide P25) TiO_2 followed first order kinetics with half-lives of 42.8, 11.0, 5.0 and 2.7 min for TOCl (Cl_2), TOBr, TOCl (NH_2Cl), and TOI formed by fulvic acid. The TOX photocatalytic degradation rates were in the order of TOI > TOCl (NH_2Cl) > TOBr > TOCl (Cl_2). The results also showed that hydrophobic and MW > 1 kDa fractions of TOCl (Cl_2) are more susceptible to the photocatalytic process than hydrophilic and MW < 1 kDa. This indicated that the unidentified group of DBPs (UTOX) are more degradable via $^{\bullet}OH$ radial oxidation mechanism in comparison to known DBPs such as THMs and HAAs. The addition of H_2O_2 at low concentrations (2-15 mg/L) to the photocatalytic process increased TOCl (Cl_2) degradation by generating more $^{\bullet}OH$ radical. However, at higher concentrations (30-60 mg/L) TOCl (Cl_2) degradation was inhibited due to scavenging of $^{\bullet}OH$ radicals and competing over sunlight absorption by excessive H_2O_2. The use of different commercially available TiO_2 phases including Hombikat UV100 (pure anatase) and TiOxide (pure rutile), resulted in decrease of the TOX photodegradation efficiency and the inhibition increased by the following order TiOxide > Hombikat UV100 > Aeroxide P25. The TOX photocatalytic degradation increased by factors of 1.09-1.45 when pH decreased from 9 to 5. Finally, the use of 100 mg/L of TiO_2 solar photocatalytic process

on TOCl (Cl_2) and TOCl (NH_2Cl) formed by real water and wastewater samples showed that the presence of natural water contaminants including inorganic ions and DOC can interfere and decrease the degradation efficiency of the process. Half-lives for TOCl (Cl_2) were 97.8 and 58.3 min for wastewater and drinking water, respectively, where for TOCl (NH_2Cl), 14.5 and 10.3 min.

Table 5.1: Results of batch reactions for dehalogenation of TOCl, TOBr, and TOI by natural solar-TiO_2 photocatalytic

(TiO_2 used is Aeroxide P25, pH 7.0 ± 0.2, natural sunlight exposure is 0.0 – 240.0 min, initial TOCl (Cl_2), TOCl (NH_2Cl), TOBr and TOI concentrations = 462 µg Cl/L, 50 µg Cl/L, 268 µg Br/L and 153 µg I/L, respectively)

TOX	TiO_2 (mg/L)	$k_{TiO2\ Adsorption}$ ($min^{-1} \times 10^{-3}$)	$k_{TiO2\text{-}Solar\ Photolytic}$ ($min^{-1} \times 10^{-3}$)	R^2 (TiO2-Solar Photolytic)	r_0 (mg L^{-1} min^{-1})
TOCl (Cl_2)	25	0	7.3 ± 0.3	0.997	0.18
	50	0	9.4 ± 0.4	0.967	0.47
	100	0	16.2 ± 1.1	0.961	1.62
	200	0	5.4 ± 0.4	0.918	1.08
	400	0.8 ± 0.1	3.4 ± 0.1	0.930	1.04
TOCl (NH_2Cl)	25	0	29.3 ± 1.3	0.970	0.73
	50	0	48.6 ± 1.9	0.951	2.43
	100	0	138.8 ± 5.6	0.986	13.88
	200	0	59.5 ± 1.7	0.996	11.90
	400	2.5 ± 0.2	27.8 ± 0.7	0.973	10.12
TOBr	25	0	16.7 ± 1.2	0.952	0.42
	50	0	22.6 ± 1.5	0.962	1.13
	100	0	63.3 ± 2.5	0.987	6.33
	200	0	28.3 ± 0.9	0.931	5.66
	400	1.2 ± 0.1	13.7 ± 0.3	0.902	5.00
TOI	25	0	38.2 ± 1.7	0.936	0.96
	50	0	60.6 ± 3.6	0.945	3.03
	100	0	258.2 ± 11.9	0.978	25.82
	200	0	102.0 ± 1.9	0.972	20.4
	400	3.3 ± 0.2	41.3 ± 0.7	0.965	15.2

a. Photolysis experiments date= 06/30/2016; average solar radiation= 1125 W/m^2; average temperature= 26 ºC.

b. Each first-rate constant shows the average value and 95% confidence intervals from linear regression of the individual logarithmic kinetic points.

Table 5.2: Water quality and TOX formation of real water samples

Parameter	Water Sample	
	Brookings WWTP	Brookings WTP
DOC (mg/L)	8.2	1.8
SUVA (L/mg/m)	3.6	1.9
Br^- (mg/L)	0.04	0.01
Nitrate (mg/L)	2.7	0.11
Sulfate (mg/L)	423	102
Chloride (mg/L)	758	184
Alkalinity (mg/L)	282	61
Turbidity (NTU)	0.92	0.21
Cl_2 TOX (ug/L)	836	182
NH_2Cl TOX (ug/L)	276	53

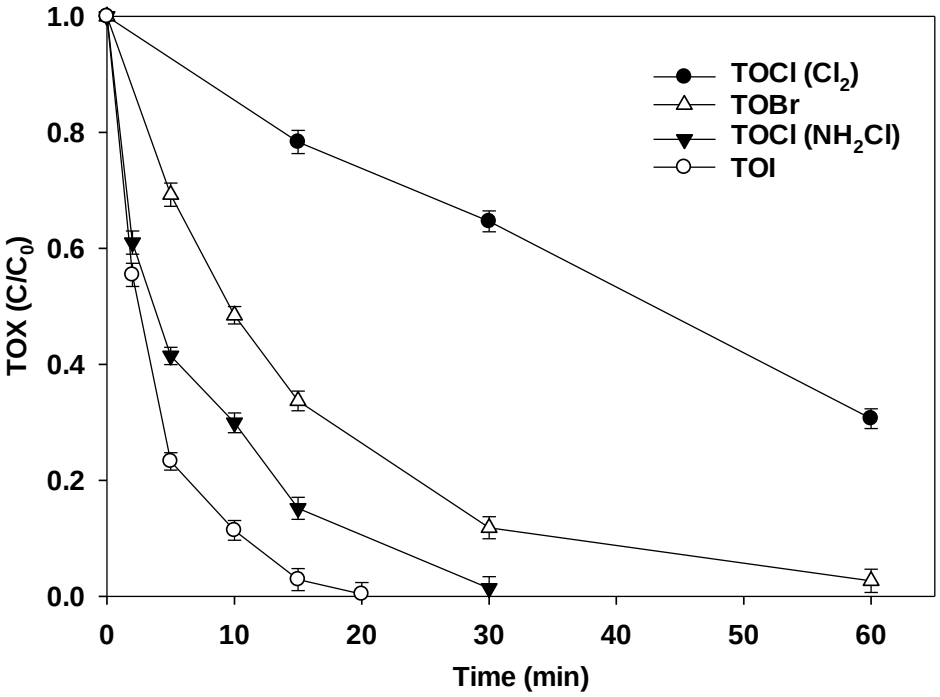

Figure 5.1: Solar photocatalytic degradation of TOX in water by TiO_2

(Reaction conditions: 100 mg/L of Aeroxide P25 TiO_2, pH 7.0 ± 0.2. Error bars show standard deviations obtained from duplicate experiments)

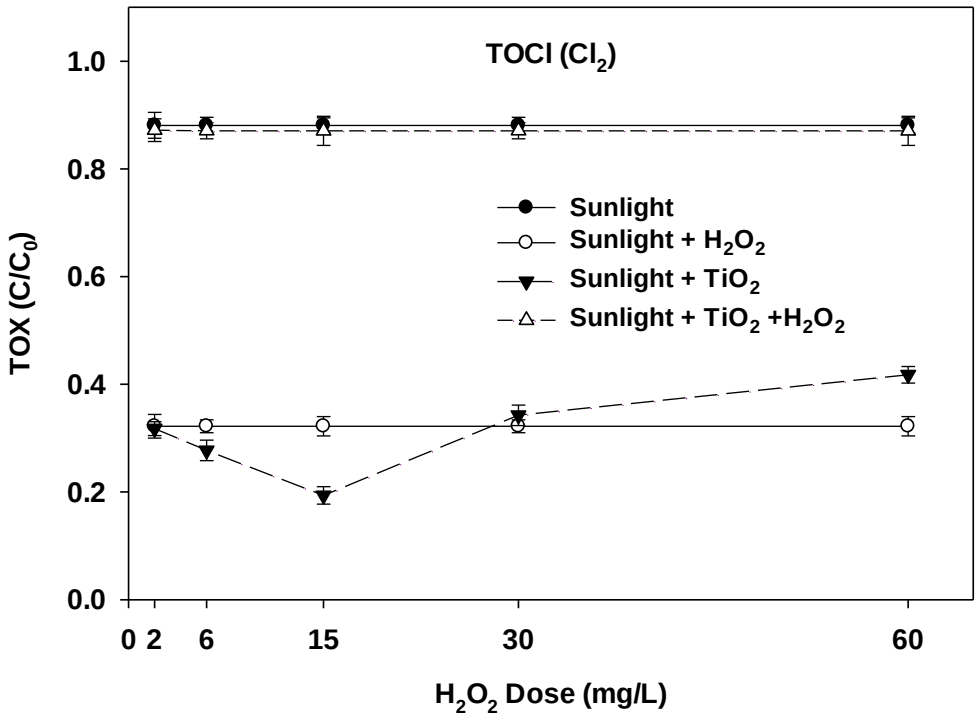

Figure 5.2: Effect of H_2O_2 on photocatalytic degradation of TOCl (Cl_2) in presence of TiO_2

(Reaction conditions: 100 mg/L Aeroxide P25 TiO_2, pH 7.0 ± 0.2, photolysis time = 60 min. Error bars indicate standard deviations obtained from duplicate experiments)

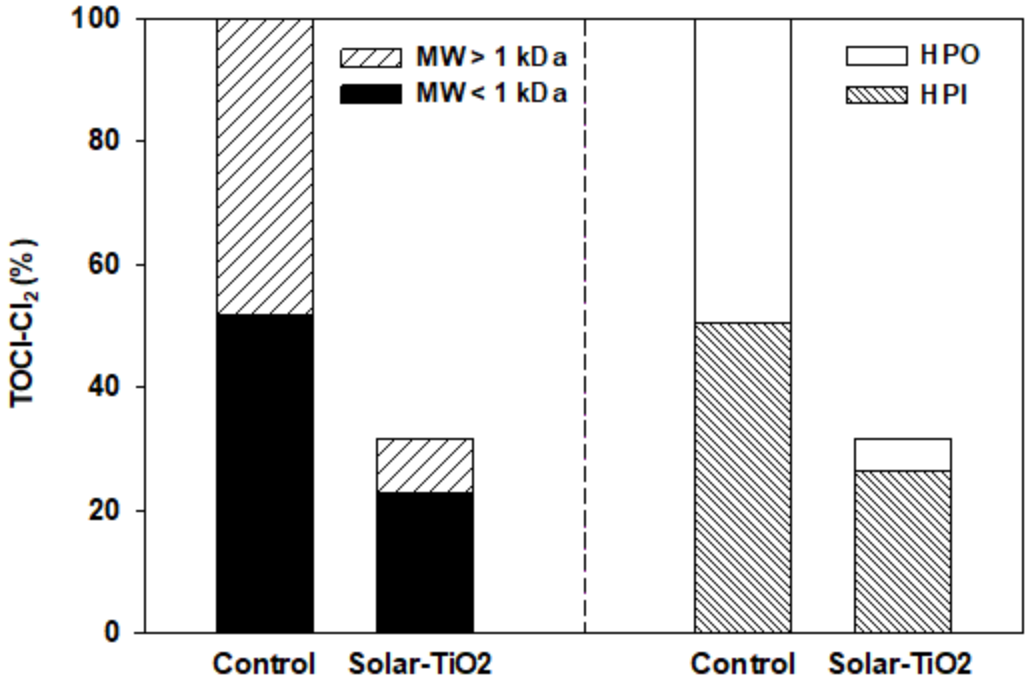

Figure 5.3: Solar photocatalytic degradation of TOCl (Cl_2) fractions in water at the presence of TiO_2

(Reaction conditions: 100 mg/L Aeroxide P25 TiO_2, pH 7.0 ± 0.2, photolysis time = 60 min.)

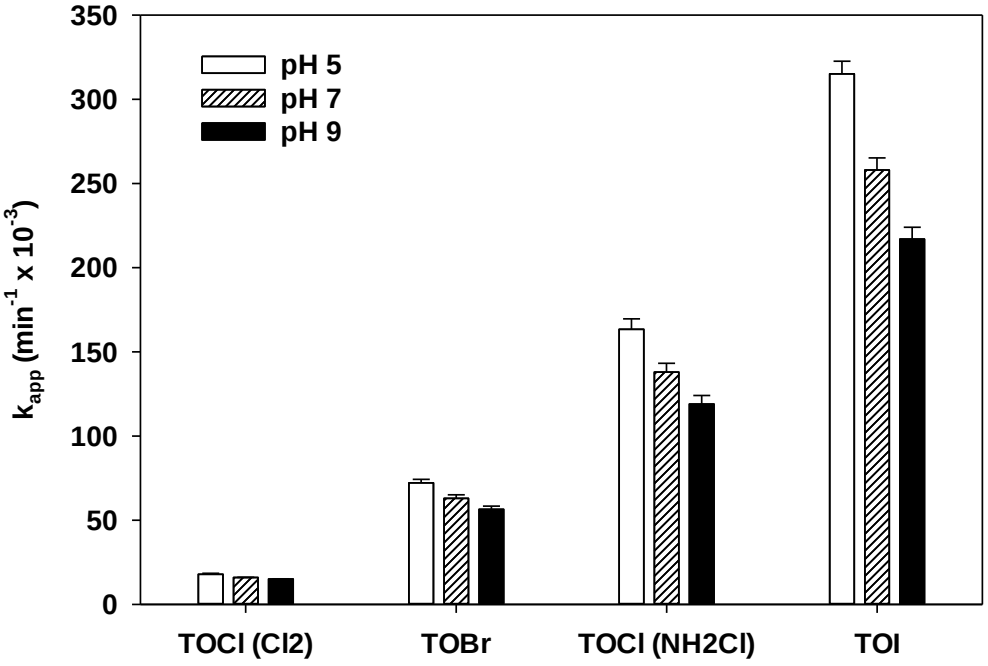

Figure 5.4: Effect of varying pH on TOX solar photocatalytic degradation kinetics by TiO_2

(100 mg/L Aeroxide P25 TiO_2; Error bars show standard deviations obtained from duplicate experiments)

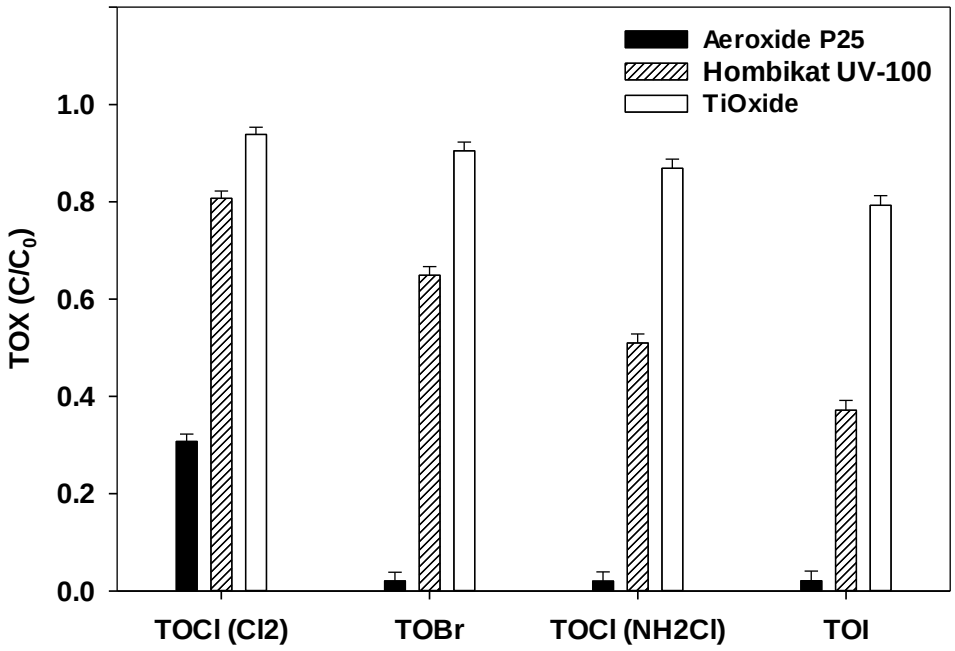

Figure 5.5: Effect of TiO_2 phase identity on TOX solar photocatalytic degradation

(Reaction conditions: TiO_2 concentration is 100 mg/L, pH 7.0 ± 0.2, Error bars show standard deviations obtained from duplicate experiments)

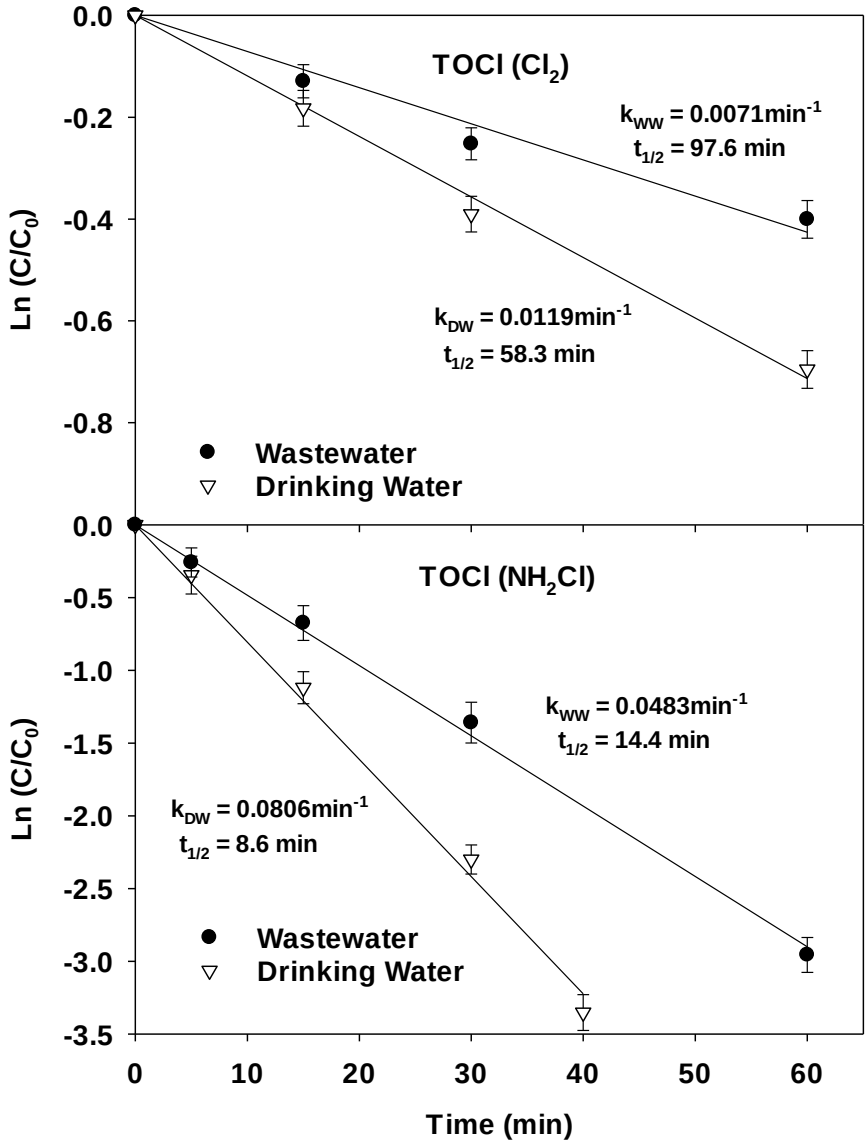

Figure 5.6: Effect of natural water matrix on solar-TiO_2 photocatalytic degradation kinetics of TOX produced by real drinking water and wastewater samples

(Reaction conditions = 100 mg/L Aeroxide P25 TiO_2. Error bars indicate standard deviations obtained from duplicate experiments)

CHAPTER SIX
DISINFECTION BYPRODUCTS REMOVAL USING NATURAL SOLAR PHOTO-FENTON

Abstract

The goal of this paper is to investigate the applicability of using a modified solar-fenton treatment to degrade disinfection byproducts (DBPs) in water and wastewater treatment plant effluents at neutral pH. Ethylenediamine-N,N′- disuccinic acid (EDDS) was used as a chelating agent to stabilize and solubilize iron at high pHs. Photo-fenton experiments were performed outdoor under natural sunlight irradiation. Total organic chlorine (TOCl) and bromine (TOBr) formed by fulvic acid exhibited rapid degradation in first 15 min and the degradation rates were in the order of TOCl(NH_2Cl) > TOBr > TOCl(Cl_2). Generally, individual DBPs were persistent to the process except for trichloronitromethane (TCNM) and monoiodoacetic acid (MIAA) with 96 and 93% removal in 1-hr of illumination. The presence of different natural water contaminates tend to inhibit DBPs degradation by the photo-fenton process, and the degree of inhibition follows the order of Cl^- (1000 mg/L) > HA (30 mg/L) > SO_4^{2-} (1000 mg/L). Additionally, the presence of alkalinity in water and wastewater effluents also decrease the degradation of TOX, but the rate depends on the concentrations of other scavenger $^{\bullet}OH$ radicals naturally exist in the waters and the input TOX concentration. The use of EDDS solar fenton process was more efficient for TOX degradation in water and wastewater effluents in comparison to the conventional solar fenton process at pH 3.0.

6.1 Introduction

In recent years, municipal wastewater effluent has been progressively used as an alternative water source to make up for the water shortage in drinking water supplies through water reuse programs, including recycling and reclamation practices (Rodriguez et al. 2009). The use of those programs is expected to further increase in the future due to the rapid increase in population and economic growth. In addition to the planned water reuse, inadvertent or accidental reuse of municipal wastewater effluent has been in operation for many years. Although the benefits of using of municipal wastewater effluent to augment drinking water resources are well known and recognized, wastewater effluent also contains a high concentration of contaminants that can cause health risks to the public and aquatic life (Snyder et al. 2003).

The addition of chlorine to wastewater effluent to deactivate microorganisms is a critical process in municipal wastewater treatment plants (MWTPs). This disinfection process can prevent the wide spread of waterborne diseases that can cause serious health concerns. When chlorine is added to the treated water effluent, it can react with the naturally existing organic materials leading to the formation of the toxic disinfection byproducts (DBPs) including trihalomethanes (THMs), haloacetic acids (HAAs), halonitromethanes (HNMs), haloacetonitriles (HANs), haloacetamides, nitrosamines, and total organic halogen (TOX) (Hua and Reckhow 2008a, Krasner et al. 2009, Mitch and Sedlak 2002, Yang et al. 2005). Additionally, due to the presence of bromide ions in wastewater effluent from industrial discharges, chlorine can oxidize bromide and iodide to bromine and iodine, which subsequently react with effluent organic matter to form brominated and iodinated DBPs. Research has shown that brominated and iodinated

DBPs are more cytotoxic and genotoxic than their chlorinated analogues (Plewa and Wagner 2009). This has raised concerns about the potential health risks of DBPs on the public and aquatic ecosystem.

Among the advanced technologies that may lead to reduce the concentrations of DBPs are the advanced oxidation processes (AOPs). Those processes can mineralize organic content leading to form CO_2 and inorganic acids as final products through the generation of hydroxyl radicals ($^{\bullet}OH$) that have very high oxidation potential of 2.8 mV (Malato et al. 2009). Solar Photo-Fenton process which produces $^{\bullet}OH$ radicals by homogeneous photo-catalysis with Fe(II/III), sunlight, and H_2O_2, has emerged as a promising energy-efficient process by using natural solar energy as a light source to reduce operational costs effectively to make it commercially and environmentally friendly(Gernjak et al. 2006, Klamerth et al. 2010, Trovó et al. 2009). One major drawback, that it requires low pH (< 3.0) to operate effectively, since iron precipitates at higher pH, therefore, if this process is going to implemented at water treatment plants, effluent pH need to be neutralized before discharge or reuse (Pignatello et al. 2006). Thus, the salt content would arise, which would be negative for certain purposes such as irrigation.

To overcome this issue, complexing agents can be used which are able to from soluble photo active species at neutral pH (Clarizia et al. 2017). Such agents are not available normally in municipal wastewater effluents, therefore they must be added during the tertiary treatment. If so, those agents should have specific characteristics where they do not pollute the environment, increase the toxicity and reduce the biodegradability of the water effluent. Aminopolycarboxylic acids (APCAs) are one of

the complexing agents that tend to form stable water-soluble complexes with metal ions specifically iron in a wide pH range ($3.0 < pH < 8.0$) (Huang et al. 2012, Miralles-Cuevas et al. 2018, Wu et al. 2014). Ethylenediamine-N,N'-disuccinic acid (EDDS) is a common synthesized substance in APCA group and structural isomer for EDTA(Li et al. 2010). Additionally, it has been reported to be both biodegradable (Zhang et al. 2008) and environmentally safe and can form photo-active iron soluble species at neutral pH.

With the rapid increase in using water reuse programs, the need to design an advanced technology that have the capability to clarify water from the hazardous DBPs to protect the public health and the aquatic ecosystem. The overall goal of this study is to determine the degradation efficiency of total organic chlorine (TOCl) and bromine (TOBr) and individual DBPs by photo-fenton process under natural sunlight irradiation conditions. In this study, commercial organic extract (fulvic acid), real municipal wastewater (WW) and drinking water (DW) were used as precursors to produce DBPs using chlorine, chloramine in the presence of bromide. EDDS was used as a chelating agent to allow the photo-fenton process to be conducted under neutral conditions and the results were compared to the classical photo-fenton at pH 3.0 results. The impact of Fe(III) dose, H_2O_2 dose, EDDS, and pH on the degradation of TOX and individual DBPs were evaluated. In addition, chloride, sulfate, nitrate, humic acid and alkalinity were varied during the experiments to simulate a wide range of water quality conditions for water reuse. The results of this research will help us determine the applicability of using EDDS solar photo-fenton process as a tertiary treatment in MWTPs to reduce the concentrations of hazardous wastewater-derived DBPs to protect drinking water supplies.

6.2 Methods and Materials

6.2.1 Preparation of TOX and DBP Samples

The TOX formation in this experiment was conducted using solutions of Suwannee River Fulvic Acid (SRFA), a wastewater effluent sample collected after filtration process from Brookings MWTP, SD, and a filtered water effluent sample from Brookings Water Treatment Plant (WTP), SD. The chemicals used in this experiment were American Chemical Society grade and purchased from Fisher Scientific (Fairlawn, NJ) unless otherwise noted. All solutions were prepared using nano-pure water (18 MΩ-cm) from Barnstead NANOpure system. SRFA was purchased from the International Humic Substances Society and dissolved in water to make a concentration of 3.0 mg/L of dissolved organic carbon (DOC). Afterward, DOC samples were treated using three different types of oxidants including chlorine, monochloramine and bromine to produce TOCl (Cl_2), TOCl (NH_2Cl) and TOBr, respectively. Doses were selected as follow: 3.0 mg/L as Cl_2, 0.4 mg/L as Cl_2 and 2.0 mg/L as Br_2, respectively. The oxidation experiments were performed in 300 mL chlorine-demand free glass bottles and the pH for the samples were adjusted to 7.0 ± 0.2 using sulfuric acid and sodium hydroxide. After the addition of each oxidant, bottles were stored in 20 ℃ incubator in dark for 72 h. Those specific experimental conditions were chosen to make sure no residual left in the samples at the end of 72 h incubation time. Chlorine and bromine stock solutions were prepared by diluting sodium hypochlorite solution (4-6%) and bromine solution (>99.5%, Sigma Aldrich (St. Louis, MO)) in water, respectively. Monochloramine stock was prepared using a method in a previous study (Abusallout et al. 2017). The measured TOX concentrations after incubation were 432 ± 16 µg Cl/L, 50 ± 4 µg Cl/L and 288 ± 9 µg Br/L for TOCl (Cl_2), TOCl (NH_2Cl) and TOBr, respectively.

Furthermore, chlorine and chloramine were added for the WW and DW samples to produce TOX samples for the solar photo-fenton experiment. Doses selected for WW were 8 mg/L and 0.8 mg/L and for DW 2.5 mg/L and 0.35 mg/L for chlorine and chloramine, respectively. Table 6.1 shows the TOCl (Cl_2) and TOCl (NH_2Cl) results after 72 h of incubation for both WW and DW samples. Alkalinity was stripped from the WW and DW samples for further tests by addition of sulfuric acid without reducing the pH significantly. Desired final alkalinity concentration was less than 5 mg/L as $CaCO_3$.

A total of 13 DBPs were selected for the experiment. Two THMs (chloroform, bromoform), seven HAAs (trichloro-, dichloro-, monochloro-, tribromo-, dibromo-, monobromo- and monoiodoacetic acid (TCAA, DCAA, MCAA, TBAA, DBAA, MBAA and MIAA, respectively)), chloral hydrate (CH), dichloroacetamide (DCAcAm), dibromoacetonitrile (DBAN) and trichloronitromethane (TCNM). All DBPs were purchased from Sigma Aldrich (St. Louis, MO). The concentration selected for each of DBP was 200 ± 10 □g/L as Cl, Br, or I for chlorinated, brominated and iodinated species. Each DBP was dissolved in water except for bromoform, chloroform, DBAN and TCNM where dissolved in acetone since they have low solubility in water. pH was adjusted for the DBP samples to 7.0 ± 0.2 using sulfuric acid and sodium hydroxide.

6.2.2 Natural Solar Photo-Fenton Experiments

The natural solar photo-fenton experiments were conducted using 60 mL test tubes. The details about the reactor and tubes were discussed in previous studies (Abusallout and Hua 2016a, b). The outdoor natural solar photo-fenton experiments were performed between May and September of 2017 on cautiously selected sunny days. The solar exposure interval for each set of experiment was between 11:30 am to maximum of

3:30 pm and the natural sunlight intensity was measured on site using a photometer (Seaward 396A916, Tampa, FL) every 15 min. The average sunlight intensity and temperature were measured to be 1108 ± 67 W/m^2 and 27 ± 2 ℃, respectively, during the photo-fenton experiments. Additionally, clouds were monitored during the solar exposure duration and the time was extended if necessary to reach the 2 h solar exposure.

Five sets of experiments were conducted to evaluate the performance of EDDS natural solar photo-fenton process on the degradation of individual DBPs and TOX species. The first experiment investigated the degradation of TOCl (Cl_2), TOCl (NH_2Cl) and TOBr in water under a specific selected dose of Fe^{3+}: EDDS (based on preliminary testing) and the following parameters were monitored during the experiment: Fe^{3+} concentration, H_2O_2 consumption, pH variation and DOC removal for each of the TOX species. The second experiment examined the stability of individual chlorinated, brominated and iodinated DBPs in water. Each of TOX and DBP samples was subjected to natural solar irradiation for 120 min at adjusted pH of 7.0 ± 0.2. In the third experiment, the investigation examined the effect of natural water contaminates on the degradation efficiency of DBPs by EDDS solar photo-fenton process. The contaminates included alkalinity (HCO_3^-/CO_3^{2-}), chloride (100-1000 mg/L), sulfate (100-1000 mg/L), nitrate (5-20 mg/L) and humic acid (10-30 mg/L). Sodium chloride, sodium sulfate, potassium nitrate and Suwannee river humic acid (SRHA) were added separately to sample tubes to achieve the targeted levels. Afterwards, samples were exposed to natural sunlight for 90 min at pH 7.0 ± 0.2. The last experiment compared the degradation of TOCl (Cl_2) and TOCl (NH_2Cl) in WW and DW using conventional solar photo-fenton at pH 3.0 and modified EDDS solar photo-fenton process at pH 7.0.

6.2.3 Experimental Setup and Procedure

When TOX and DBPs samples were ready for the experiments, samples were treated according to the following procedure:

1. For the modified EDDS solar photo-fenton process, H_2O_2 was added to the 300 mL bottles (containing TOX or DBPs) at initial concentration of 50 mg/L and homogenized for 15 min. Afterwards, a dose of 1:2 of the Fe^{3+}: EDDS solution was added and mixed for another 15 min. Then, a sample was taken immediately to evaluate the effect of fenton in dark. The Fe^{3+}: EDDS stock was made by mixing iron (III) sulfate with EDDS at pH 3. Finally, samples were transferred into the photolysis tubes and exposed to natural sunlight to start the solar photo-fenton process. Control samples were added next to the previous samples to evaluate the effect of natural sunlight alone on the stability of TOX and DBPs. For the conventional solar photo-fenton, the same steps were followed as previously described, but pH was lowered to 3 before exposing samples to natural sunlight.
2. For the first 30 min of sunlight exposure, samples were taken as follow: 2, 5, 10, 15 and 30 min and for the remaining 90 min samples was taken every 30 min. Additionally, H_2O_2 was added as necessary to keep the concentration at 50 mg/L to allow the photo-fenton reaction to continue.
3. At the end of solar exposure time, samples were covered from sunlight using aluminum foil and immediately 5 mL of sample was diluted to 40 mL for DOC measurement. Another 5 mL was taken for pH and iron measurements respectively and a final 5 mL drawn for the measurement of H_2O_2 consumption.

For TOX and DBPs measurement, immediately a 100 µL of bovine lever catalase (used as purchased from Sigma Aldrich) was added to quench any H_2O_2 residual (one unit of catalase can consume about 1µm of H_2O_2 per minute at pH 7.0), then pH was dropped to 2 using nitric acid and incubated at 4 °C for further TOX analysis.

6.2.4 Analytical Procedures

Chlorine and bromine residuals were measured using DPD ferrous titrimetric method (Rice et al. 2012). TOX and DBPs samples were acidified to pH 2 and stored at 4 °C before analysis using Mitsubishi TOX-100 Analyzer (Cosa Xentaur Inc., Norwood, NJ). The TOX concentrations were quantified by an adsorption-pyrolysis-titration method. This method was based on standard method 5320 B with minor modifications (Rice et al. 2012). TOX recovery tests have been performed on individual DBPs including bromoform, trichloroacetic acid, dichloroacetic acid, dibromoacetic acid, monobromoacetic acid, dichloroacetonitrile, dibromoacetonitrile, chloral hydrate and trichloronitromethane. The use of the this TOX method showed recoveries between 95% and 105% for the mentioned DBPs which are very similar to a previous study (Hua and Reckhow 2006). Additionally, SRFA solutions were analyzed for the presence of halogens including bromide and iodide, but no traces were found for any of them in the SRFA, and since pure chlorine, bromine and monochloramine were used for the experiments along with SRFA solutions, TOX species were identified as TOX-halogen specific concentrations. Chloride, bromide, iodide, nitrate and sulfate ion concentrations were analyzed using a DX-500 ion chromatography system (Dionex, Sunnyvale, CA) equipped with a conductivity detector (CD-20, Dionex).

DOC concentrations were analyzed using a Shimadzu TOC-5000 Analyzer (Shimadzu Corp., Kyoto, Japan) according to Standard Method 5310 B (Rice et al. 2012). H_2O_2 concentrations were measured during the experiments by spectrophotometry using titanium(IV) oxysulfate according to DIN 38402H15 and the total iron determination was achieved by using 1,10-phenantroline method following ISO 6332.

6.3 Results and Discussion

6.3.1 The Degradation of TOX in Water by Traditional Fenton-Like Reactions

Experiments were conducted for the removal of TOCl (Cl_2), TOCl (NH_2Cl) and TOBr in water at low iron (Fe^{3+}) concentration of 0.09 mM and EDDS of 0.2 mM (1:2 ratio Fe^{3+}: EDDS). This dose was selected based on preliminary tests that determined the most efficient Fe^{3+}: EDDS concentration based on highest TOX removal with minimum H_2O_2 and iron consumption as possible (Table 6.2). Furthermore, the dose was assured not to be high enough that it can reduce the degradation efficiency by scavenging $^{\bullet}OH$ radicals.

Fig 6.1 shows the effect of EDDS solar photo-fenton process on TOCl (Cl_2), TOCl (NH_2Cl) and TOBr in water over 90 min of natural sunlight exposure. The period between -15 and 0 min represent sample in dark (before sunlight irradiation) but after the addition of H_2O_2 at initial concentration of 50 mg/L and Fe^{3+}:EDDS of 1:2. The results in dark showed some degradation of 10.8, 15.5 and 22.1%, respectively. All TOX species exhibited increase in DOC due to the addition of EDDS (from initial 3.0 to 48.5 mg/L). Afterwards, insignificant changes for DOC, pH, soluble iron and H_2O_2 before exposing the reactor to natural sunlight. This observed degradation in the dark stage for the TOX species is due to the Fenton-like process, which in case of Fe^{3+} and EDDS is partially

efficient. Fenton degradation was very quick and did not proceed further until the samples were exposed to the sunlight, since Fe^{3+} reduction to Fe^{2+} was very limited without sunlight irradiation.

6.3.2 The Photodegradation of TOX in Water by Modified EDDS Solar Photo-Fenton Reactions

For TOCl (Cl_2) (figure 6.1a), after the dark stage, samples were exposed to natural sunlight starting at 0 to 120 min. The results showed overall degradation of TOCl (Cl_2) up to 67.3%, where 40% of the total decomposition was in the first 15 min, but afterward slowed down and then the process almost inhibited after 90 min. DOC showed a similar behavior where in the initial 15 min mineralization was 30.7% and reached maximum of 53.7% by 90 min. This degradation in TOX and DOC was incorporated with rise in H_2O_2 consumption reaching 99.1 mg/L after 90 min, 79.3 mg/L was only in the initial 15 min.

Fig 6.1b presents the profile for TOBr degradation and the incorporated changes in DOC, pH, and H_2O_2 consumption. The results showed promising degradation in short period of time for the toxic brominated TOX, where total degradation of 87.9% was achieved in 90 min after illumination, 55.2% was degraded in the initial 15 min. DOC was also observed to have a significant degradation of 57.6% in 90 min of natural sunlight irradiation. On the other hand, the degradation of TOBr consumed total of 96.6 mg/L of H_2O_2 after 90 min, which is very similar amount to what we observed for TOCl (Cl_2).

Finally, the degradation of TOCl (NH_2Cl) was also investigated using the modified EDDS solar photo-fenton process (figure 6.1c). The results showed that TOCl (NH_2Cl) was the most degradable TOX with 90.1% in only 60 min after natural sunlight

illumination, then the process slow down significantly. DOC was also mineralized in a similar behavior to the DOC during TOCl (Cl_2) and TOBr experiments, where it degraded up to 56.1% in 60 min. Additionally, this high degradation of TOCl (NH_2Cl) required a high concentration of H_2O_2 to be available during the sunlight irradiation, typically about 94.2 mg/L after 60 min. Similarly to TOCl (Cl_2) and TOBr results, most of the degradation of TOCl (NH_2Cl), DOC and development of H_2O_2 has occurred in the initial 15 min of natural sunlight illumination with 78.2%, 48.7% and 79.2 mg/L, respectively.

During the three TOX experiments, pH did not change significantly and were stable around 7.0 during illumination. Moreover, control samples showed insignificant degradation (< 8%) for all the TOX species by natural solar photolysis, similarly to what the authors have detected in previous research (Abusallout and Hua 2016a).

In general, the use of the EDDS modified solar fenton process at pH 7 for the degradation of different TOX species showed very promising results. TOCl (Cl_2), TOBr and TOCl (NH_2Cl) were very sensitive to the process and degraded extremely in short period of time and TOX stability followed the order of TOCl (Cl_2) > TOBr > TOCl (NH_2Cl). However, the degradation rate of TOX species was proceeded in two steps: 1) The duration between 0 to15 min and 2) After 15 to 90 min.

In the initial 15 min, all TOX species exhibited more than 40% degradation and it incorporated with H_2O_2 consumption of 72.4 ± 3.1 mg/L with insignificant iron (not shown) and EDDS removal. These ideal conditions can clearly maximize the formation of $^{\bullet}OH$ radicals that led to the initial substantial removal observed. Afterwards, between 15 and 90 min, TOX degradation rate decreased and the removal was less than 28% and

H_2O_2 consumption dropped to 19.3 ± 1.3 mg/L. This decrease in degradation efficiency is due to the decomposition of EDDS with an average of 55.8% after 90 min, thus led to the precipitation of free Fe^{3+} in its hydroxide form due to the high pH. This incorporate well with our results where we observed 25% reduction in free iron concentration after 90 min. Additionally, at neutral pH, literature showed presence of different forms of Fe^{3+}-EDDS complexes including $Fe(OH)EDDS^{2-}$ and $Fe(OH)_2EDDS^{3-}$ that are less photochemically efficient that accumulate in the reactor over time, therefore hindering the formation of $^{\bullet}OH$ significantly later in the process.

The observed order of degradation for the TOX species was not only based on the parameters of the EDDS process itself, but also based on the initial TOX concentration. The results showed that increasing the input TOX concentration has reduced the removal efficiency. The high concentration of TOX require higher amount of $^{\bullet}OH$ radicals to reach effective removal and since the other operating parameters are in constant level, thus, $^{\bullet}OH$ radicals generation are also constant. Additionally, when initial TOX is too high, it competes with the hydrogen peroxide for the sunlight absorption, therefore, hindering the formation of $^{\bullet}OH$ radicals. The observed high TOX degradation could be attributed to the nature of the unknown fraction of TOX (UTOX). UTOX consist mostly high molecular weight aromatic compounds that contain double bonds and aromatic rings (Hua and Reckhow 2008b), which are favored by $^{\bullet}OH$ radicals attacks over aliphatic compounds (Gligorovski et al. 2015).

6.3.3 Degradation of individual DBPs by EDDS solar photo-fenton process

Fig 6.2 shows the ratios of each DBP final TOX concentration (C) to initial concentration (C_0) at different sunlight exposure times during EDDS solar photo-fenton

process. DBPs stability under Fenton-like process was investigated in dark after the addition of 50 mg/L H_2O_2 and 1:2 Fe^{3+}:EDDS ratio. The average reduction of each DBP concentration was less than 10% during incubation in the absence of natural sunlight, suggesting that the limited $^{\bullet}OH$ formed from Fenton-like process in dark was not sufficient to reduce DBPs stability effectively without natural sunlight irradiation. Furthermore, in the presence of the natural sunlight only, DBPs exhibited insignificant degradation except for TCNM with 20% removal after 1-hr.

In this experiment, DBPs were investigated separately and classified into two groups: neutral DBPs including chloroform, bromoform, CH, DCAcAm, DBAN and TCNM, and acidic DBPs including TCAA, DCAA, MCAA, TBAA, DBAA, MBAA and MIAA. Fig 6.2a shows the degradation among the neutral DBPs separately, DCAcAm (8.9%) and chloroform (20.1%) demonstrated a relative high stability after 1-hr of EDDS solar fenton process. Haloacetamides are class of emerging nitrogenous DBPs that have been reported to be two orders of magnitude more cytotoxic that HAAs (Plewa et al. 2007). The results indicate that the molecular structure of DCAcAm is resistant to $^{\bullet}OH$ radical attacks formed by EDDS solar fenton process, therefore, another degradation methods need to be developed to remove it from wastewater effluent to protect the aquatic life and public health. Similarly, chloroform showed high stability after 1-hr of EDDS solar fenton process with only 20.1% removal, this degradation was not expected, but a recent study by Chaung et al. 2016(Chuang et al. 2016a) where they measured the $^{\bullet}OH$ reaction rates for chloroform ($k_{\bullet OH} = 5.4 \times 10^7\ M^{-1}S^{-1}$) to be higher than some other halogenated DBPs including HAMs. Therefore, based on our findings, we expect the following dehalogenation pathway for chloroform by EDDS solar fenton process: First,

$CHCl_3$ reacts with •OH and produce organic free radicals •CCl3 (R1) (Tang and Tassos 1997) that subsequently reacts with another •OH to form trichloromethanol (CCl_3OH) (R2) (Oturan et al. 2018). Trichloromethanol then decompose in water into phosgene (R3) (Brudnik et al. 2008) that quickly hydrolyzed in water (R4) (Mertens et al. 1994).

$$CHCl_3 + \bullet OH \rightarrow \bullet CCl_3 + H_2O \quad (R1)$$

$$\bullet CCl_3 + \bullet OH \rightarrow CCl_3OH \quad (R2)$$

$$CCl_3OH \rightarrow CCl_2O + Cl^- + H^+ \quad (R3)$$

$$CCl_2O + H_2O \rightarrow CO_2 + 2Cl^- + 2H^+ \quad (R4)$$

R2 reaction is not expected to be predominant pathway, due to the major presence of soluble free iron ions that will scavenge chloroform radical (•CCl_3) by oxidation, reduction or dimerization leading to the formation of CCl_3^+, CCl_3^- and $Cl_3C\text{-}CCl_3$, respectively (Sheldon 2012). Consequently, this competition led to the nonproductive decomposition of chloroform forming chlorinated intermediates that can still pose risks to the public health. Appreciable dehalogenation extents after 1 h of EDDS solar fenton process were observed for chloral hydrate (49.2%), bromoform (65.7%), DBAN (82.3%) and TCNM (95.7%). It seems that •OH radicals generated in the process is effective in removing this group of neutral DBPs in short period of time. This is consisting with earlier studies reported similar significant degradation by •OH radicals generated by AOPs(Chuang et al. 2016a, Cole et al. 2007, Prousek et al. 2007, Tang and Tassos 1997). However, our results demonstrated that TCNM was the most degradable DBP by EDDS solar photo-fenton. This could be overestimated, since TCNM showed 20% degradation in the control sample after 1 hr of natural solar photolysis alone (Abusallout and Hua

2016b). That's mean that the degradation observed was combined by •OH radical attacks and dehalogenation by sunlight.

Fig 6.2b shows the degradation of HAAs by EDDS solar photo-fenton process during 1-hr of reaction time. In general, results demonstrated that chlorinated and brominated HAAs are relativity stable under photo-fenton process including TCAA (6.8%), TBAA (9.2%), DCAA (15.7%), DBAA (17.6%), MCAA (19.3%) and MBAA (21.8%). On the contrary, iodinated HAAs represented by MIAA was degraded up to 93.6% at 1-hr of reaction time, 60% of the removal achieved in the first 15 min. MIAA had been reported to be very toxic to mammalian cells (Plewa et al. 2004), therefore, the use of EDDS solar photo-fenton process should be ideal for the removal of MIAA during water reuse practices.

The results indicated that the HAAs degradation increased with decrease in number of halogen (mono- > di- > tri-halogenated) and size of substituted halogen (I > Br > Cl). The less halogens in HAA, the more C-H bonds are available, therefore, more degradation was observed since •OH radicals favor H abstraction (Gligorovski et al. 2015). Additionally, iodine and bromine substituents are better in leaving the groups than chlorine, since bromide and iodide ions are relatively stable and weakly basic ions than chloride ions. Therefore, this explains the degradation rate among the HAAs group. However, chlorinated and brominated HAAs are still very resistant to the EDDS solar fenton process and more research is needed to decompose those DBPs in water effluents to protect the public health.

In general, the use of EDDS solar fenton process for the removal of individual DBPs followed primary the type of a neighboring functional group associated with the

DBP that could affect the activation energy in the carbon-halogen bond. Additionally, $^{\bullet}$OH radicals are capable of abstracting the H attached to the α carbon, and the H from different reaction sites in the functional groups including N-H (amide), O-H (alcohol)… etc. However, since this study did not investigate all DBPs to account for the effect of number and type of the halogens inside the DBP, therefore, it's very complicated to give an accurate estimation in which functional group is sensitive to the $^{\bullet}$OH radicals more than the other. However, Chuang et al 2017(Chuang et al. 2016a) developed a predation model to examine the $^{\bullet}$OH radical reaction rates with different groups of halogenated DBPs. But our results concluded that DBPs contained more iodide ions are the most reactive and degradable by $^{\bullet}$OH radical attacks, where DBPs with acetic acid group and more chloride ions are the least degradable, which it agrees with the model.

6.3.4 Effect of Sulfate, Chloride, Nitrate and Humic Acid on Individual DBPs

The presence of inorganic ions (SO_4^{2-}, Cl^- and NO_3^-) and humic substances (HA) in wastewater effluent may have a significant effect on the overall reaction rates in photo-fenton processes. Cl^- and SO_4^{2-} may decrease the degradation efficiency of the targeted organics through I) reactions with Fe^{2+} and Fe^{3+} that change the distribution and reactivity of iron species II) formation of precipitated Fe^{3+} complexes that decrease the availability of Fe^{3+} during the process and III) scavenging of $^{\bullet}$OH radicals and forming instead less reactive radicals ($Cl^{\bullet-}$ and $SO_4^{\bullet-}$)(De Laat et al. 2004, Devi et al. 2013). On the other hand, the presence of NO_3^- may increase the degradation rates through sunlight excitation of nitrate ions forming various nitrogen reactive species (NO, NO_2, etc.) and in a less degree $^{\bullet}$OH radicals that can degrade organic and inorganic compounds (Keen et al. 2012). HA present in water could have two conflicting effects on the photo-fenton

process. It could either enhance the process by acting as colloids forming stable complexes with metals (similar to EDDS) that increase the availability of Fe^{3+} ions at higher pHs , therefore increasing the formation of $^{\bullet}OH$ radicals(Klamerth et al. 2013), or inhibit the solar photo-fenton process due to filtering effect of sunlight by the organic molecules(Abusallout and Hua 2016a, b), therefore shutting off Fe^{2+}/Fe^{3+} cycle regeneration.

Fig 6.3 presents the effects of Cl^-, SO_4^{2-}, HA and NO_3^- on degradation of DBPs by EDDS natural solar photo-fenton process. As predicted, chloride and sulfate had decreased the degradation of each DBP. The inhibiting effects were similar among chloral hydrate, bromoform and DBAN where their degradation extents decreased by 13.5-18.2% and 32.4-38% for samples spiked 1000 mg/L SO_4^{2-} and 1000 mg/L Cl^-, respectively. Increased inhibiting effects were observed for high degradable DBPs including TCNM and MIAA and the degradation degrees after 1-hr of EDDS solar fenton process decreased by 25.7-27.8% and 49.8-56.9%. On the other hand, chloroform exhibited the least inhibition in degradation by SO_4^{2-} and Cl^- for 9.6% and 16.4%, respectively. Additionally, depletion in dissolved iron was measured during the experiment for all DBPs and compared to the blank samples that do not contain chloride or sulfate. The results showed 1.9 ± 0.1, 2.2 ± 0.1 and 3.0 ± 0.2 mg/L of iron removed after 1-hr of EDDS solar-fenton process by blank, 1000 mg/L SO_4^{2-} and 1000 mg/L Cl^-, respectively. This decrease in available iron affect directly the rates of H_2O_2 consumption 99 ± 7, 64 ± 9 and 47 ± 4 mg/L, respectively. It seems that the presence of high concentrations of chloride and sulfate can compete with EDDS over available Fe^{3+} in the process. Thus, favoring the formation of inactive precipitated chlorinated- and sulfated

iron complexes and reducing H_2O_2 consumption rates, $^{\bullet}OH$ radical generation and decrease the DBPs degradation efficiencies.

The addition of 30 mg/L of HA did not seem to induce the degradation of DBPs by EDDS solar photo-fenton process, instead, inhibited all degradations significantly by the sunlight screening effect. The most inhibited DBPs were the most degradable (DBAN, TCNM and MIAA) with decrease in degradation extents of 33.2-43.2%, and in a less degree for chloral hydrate, bromoform and chloroform of 14-26.9% during 1-hr of EDDS solar photo-fenton spiked with 30 mg/L HA. Finally, Fig 6.3 shows that the addition 20 mg/L NO_3^- and the expected formation of nitrate radicals did not seem to be effective against DBPs. In general, SO_4^{2-}, Cl^- and HA had higher inhibiting effects on the fast degrading DBPs than the slow degrading DBPs by EDDS solar photo-fenton. All three contaminates caused the largest reductions efficiency to TCNM, which was also the most decomposed DBP in this study. Furthermore, each of the contaminates increased the inhibiting effect of DBPs in the order of Cl^- (1000 mg/L) > HA (30 mg/L) > SO_4^{2-} (1000 mg/L).

6.3.5 Effect of sulfate, chloride, nitrate and humic acid on individual DBPs

Table 6.1 presents the water quality characteristics of the filter effluents from Brookings water and wastewater treatment plants. Due to the significant higher concentration of DOC in the MWTP sample comparing to the DWT sample, TOX formation was much higher during chlorination and chloramination. The bromide concentration in both waters was relatively low, therefore it's expected that chlorinated substituted DBPs are the major species in the TOX samples.

Fig 6.4 presents the impact of the alkalinity on the TOX formed by MWTP and DWT using EDDS natural solar photo-fenton process. The total degradation of the WWTP and DWTP TOX samples were relatively lower than what we reported previously for TOCl (Cl_2) and TOCl (NH_2Cl) formed by SRFA, due to the highly concentrated contaminates in the water effluents including chloride, sulfate, DOC and others (table 6.1). Alkalinity (HCO_3^-/CO_3^{2-}) had been reported to severely scavenge $^{\bullet}OH$ in solar photo-fenton process, therefore, reducing the degradation efficiency of the targeted compounds significantly (Klamerth et al. 2012). This is due to the high reactivity of HO• with bicarbonate, which it was evaluated at a rate constant equal to 8.5×10^6 M^{-1} s^{-1}.(Buxton et al. 1988) To assess the effect of alkalinity on the process, MWTP- and DWT-TOX samples were stripped from alkalinity and compared to TOX samples treated as received, and then subjected to 1-hr of EDDS solar photo-fenton process. The results showed decrease in degradation extents of TOX species in the presence of alkalinity in both waste- and drinking water by 15.9, 11.6, 7.1 and 3.7% for DW-TOCl (NH_2Cl), DW-TOCl (Cl_2), WW-TOCl (NH_2Cl) and WW-TOCl (Cl_2), respectively. The rate of inhibition was mainly affected by the presence of other competing $^{\bullet}OH$ scavengers including chloride, sulfate and DOC, and since DW is relativity low with those contaminates, alkalinity was the only $^{\bullet}OH$ scavenger available, therefore the inhibition was higher than WW, where those contaminates are highly concentrated. Additionally, the rate of inhibition was increased with the increase in starting TOX concentration for each sample. This has been confirmed in this experiment, since the input TOX concentrations were as follow 789, 256, 159 and 61 µg/L for WW-TOCl (Cl_2), WW-

TOCl (NH_2Cl), DW-TOCl (Cl_2) and DW-TOCl (NH_2Cl), respectively, and the increase in inhibition followed the same order.

In general, the effect of alkalinity in TOX reductions by EDDS solar fenton process is relatively low, even at high concentrations of alkalinity. This may be due to the predominate presence of superoxide radicals ($HO_2^{\bullet}/O_2^{\bullet-}$) at pH 7.0, that enhance the reduction of Fe^{3+} to Fe^{2+} in the presence of transition metals such as EDDS. This improves the photo-Fenton process significantly, especially since the reactivity of bicarbonate with superoxide radicals is insignificant comparing to $^{\bullet}OH$ radicals at any pH(Bielski and Richter 1977, Schmidt 1972).

Therefore, at neutral pH and in the presence of Fe(III)−EDDS complex, photo-Fenton process was much more efficient and the main process responsible for the organic compounds degradation.

6.3.6 Comparison of EDDS Solar Photo-Fenton At Neutral pH and Conventional Photo-Fenton Process at pH 3.0 for The Removal of TOX in Real Water

To assess if the EDDS solar photo fenton process at pH 7.0 should be preferred over other common AOPs process for the removal of TOX in real water and wastewater samples, the TOX degradation results were compared to results by the conventional photo-fenton process at pH 3.0. Fig 6.5 presents the degradation of TOCl (Cl_2) and TOCl (NH_2Cl) in real DW and WW samples after 1-hr of natural sunlight for both processes. The results showed increase in degradation for all TOX samples by EDDS solar photo-fenton process over the conventional process by 8.3 and 17.5% in DW and 21 and 39% in WW for TOCl (Cl_2) and TOCl (NH_2Cl), respectively. In WW-TOX samples, EDDS process was much more effective comparing to the conventional method where TOX was

almost completely inhibited and less than 11% degradation was observed. However, in the DW samples, some degradation was observed for both TOCl (Cl_2) and TOCl (NH_2Cl) up to 40-66.5%, but it was still lower than EDDS solar fenton process at neutral pH. It seems that the presence of EDDS is essential not only to enhance the solubility of iron ions at higher pHs, but also to bind strongly with iron, thus reducing its availability to form precipitated complexes with contaminates that highly concentrated in wastewater, thus terminating the cycle of Fe^{3+}/Fe^{2+} generation during photo-fenton process. Additionally, the concentration of superoxide radicals at pH 3.0 is negligible comparing to neutral pH (Klamerth et al. 2012), and as mentioned earlier, the more the concentration of superoxide radicals the better the $^{\bullet}OH$ radical formation. Therefore, due to those reasons, degradation of TOX species were better by EDDS solar-fenton process comparing to the conventional method at low pH.

6.4 Conclusions

The use of natural solar photo fenton process at neutral pH for removal of DBPs have shown promising results. EDDS was used as chelating agent to prevent iron species precipitation at higher pH values. The order of TOX degradation increased as follow TOCl(NH_2Cl) > TOBr > TOCl(Cl_2). However, individual chlorinated, brominated and iodinated DBPs were persistent to the process except for MIAA (93%) and TCNM (96%) within 1-h of operation. Since TOX consist of roughly 50% of the known individual DBPs, this indicated that UTOX is accountable to major observed degradation under the generated $^{\bullet}OH$ radicals by solar photo fenton process. Natural water conctinaites present in natural waters including sulfate, chloride, humic acid decrease the efficacy of solar fenton process for DBPs removal, since they tend to either react with the dissolved iron

leading to forming inactive iron species, or blocking natural sunlight from reaching the fenton reaction, thus shutting off iron recycle regeneration. Additionally, alkalinity can also inhibit TOX photodegradation by scavenging generated •OH. Therefore, cautions and consideration need to be taken before applying this treatment system for DBPs removal in water and wastewater treatment.

Table 6.1: Water quality and TOX formation of real water samples

Parameter	Water Sample	
	Brookings WWTP	Brookings WTP
DOC (mg/L)	7.7	2.1
SUVA (L/mg/m)	3.5	1.8
Br^- (mg/L)	0.05	0.01
Nitrate (mg/L)	1.3	0.08
Sulfate (mg/L)	646	122
Chloride (mg/L)	798	113
Alkalinity (mg/L)	297	69
Turbidity (NTU)	0.57	0.11
Cl_2 TOX (ug/L)	789	195
NH_2Cl TOX (ug/L)	256	61

Table 6.2: TOX, DOC, H_2O_2 and iron concentration changes after 1 hr of natural solar fenton process using different Fe^{3+} and EDDS ratios (Fe^{3+}= 5.0 mg/L)

TOX Species	Fe^{3+}:EDDS Ratio	TOX Removal (%)	DOC Removal (%)	Total H_2O_2 Consumption (mg/L)	Final Iron Concentration (mg/L)
TOCl (Cl_2)	1:1	41	55	93	4.3
	1:2	61	52	96	4.0
	1:3	49	33	160	3.7
TOBr	1:1	52	58	94	4.5
	1:2	76	55	95	3.9
	1:3	59	36	162	3.5
TOCl (NH_2Cl)	1:1	61	60	95	4.5
	1:2	87	56	97	4.0
	1:3	67	40	185	3.7

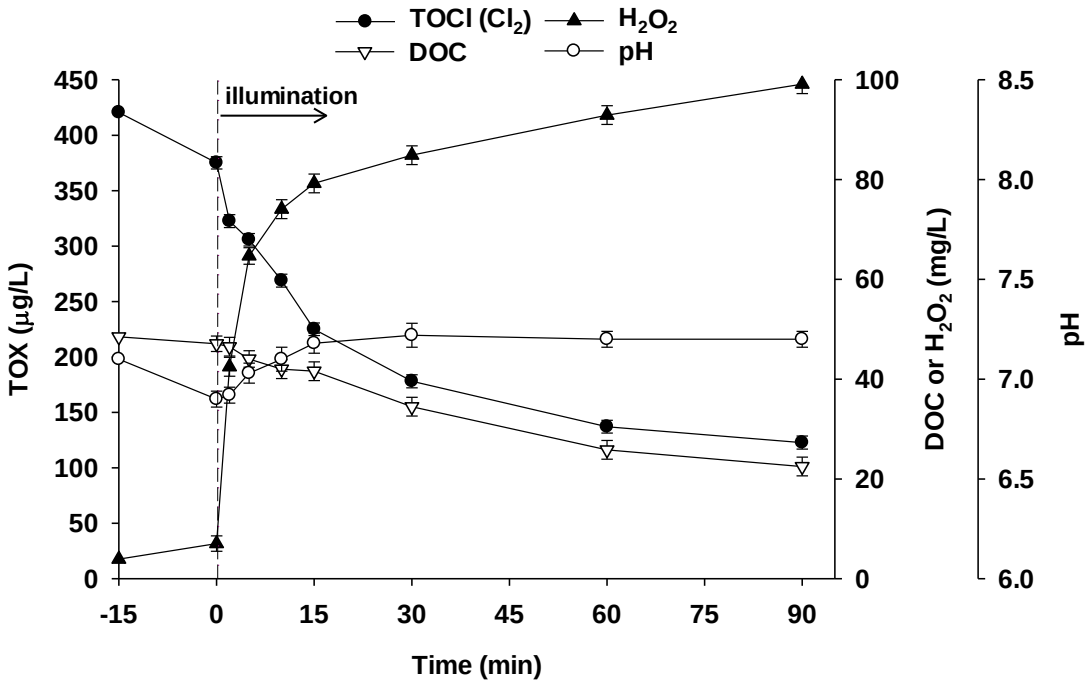

Figure 6.1a: Degradation profile for TOCl (Cl_2) formed by fulvic acid and treated with photo-fenton process under natural sunlight irradiation with 5 mg/L iron, 50 mg/L H_2O_2 and 0.2 mM EDDS at neutral pH

(Photolysis experimental conditions: date=06/25/2017, average solar radiation=1138 W/m^2).

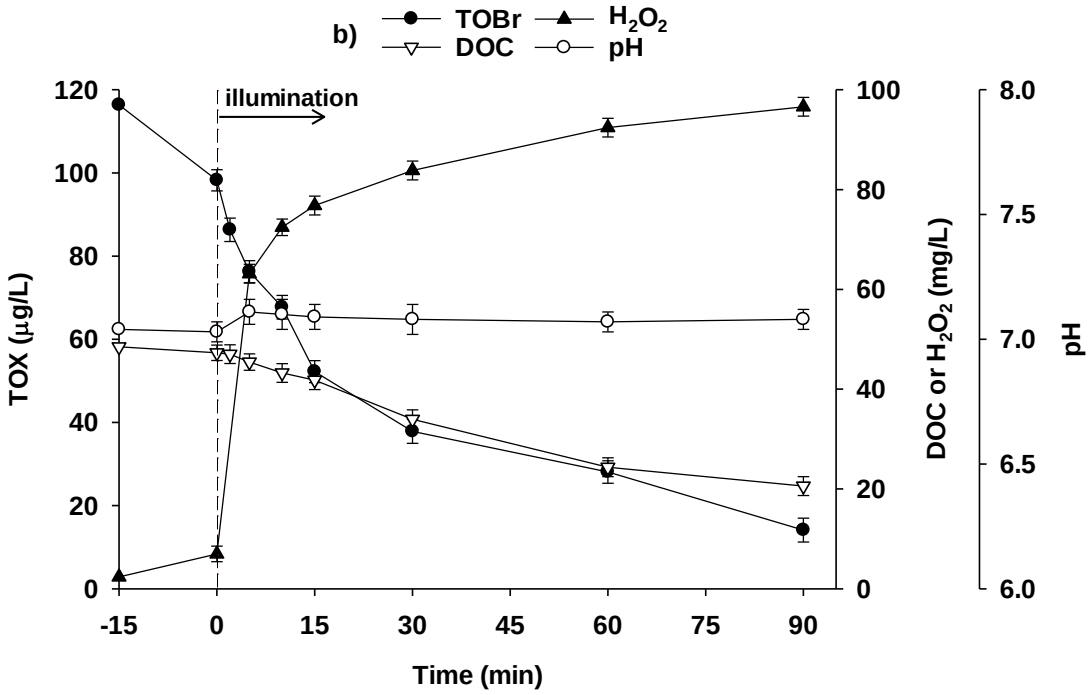

Figure 6.1b: Degradation profile for TOBr formed by fulvic acid and treated with photo-fenton process under natural sunlight irradiation with 5 mg/L iron, 50 mg/L H_2O_2 and 0.2 mM EDDS at neutral pH

(Photolysis experimental conditions: date=06/25/2017, average solar radiation=1138 W/m^2).

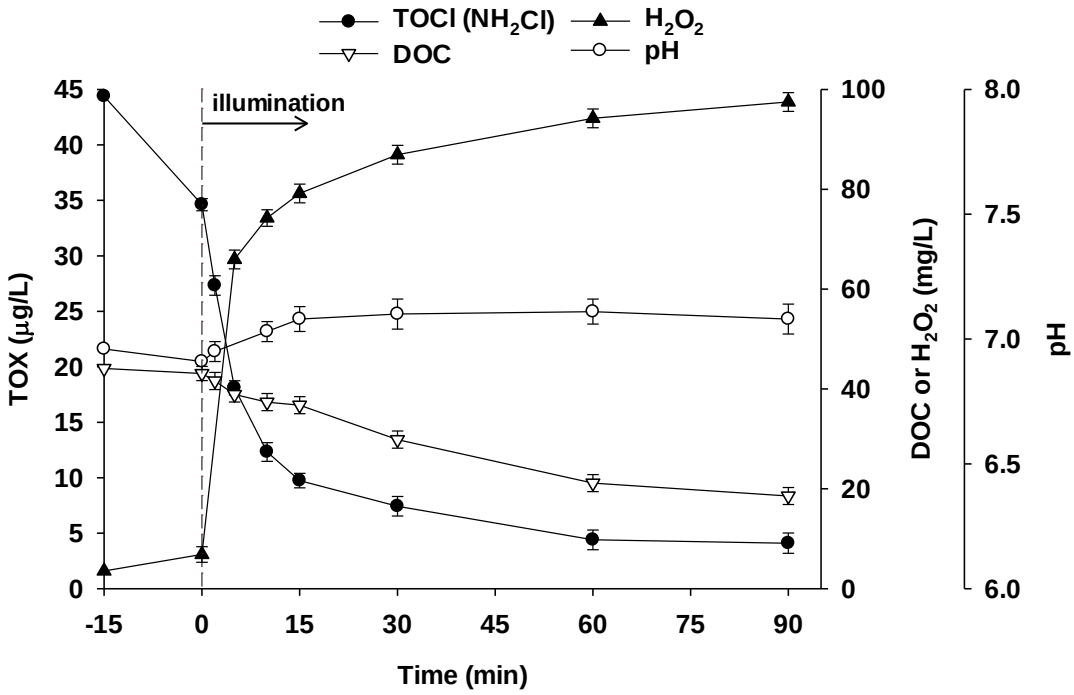

Figure 6.1c: Degradation profile for TOCl (NH_2Cl) formed by fulvic acid and treated with photo-fenton process under natural sunlight irradiation with 5 mg/L iron, 50 mg/L H_2O_2 and 0.2 mM EDDS at neutral pH

(Photolysis experimental conditions: date=06/25/2017, average solar radiation=1138 W/m^2).

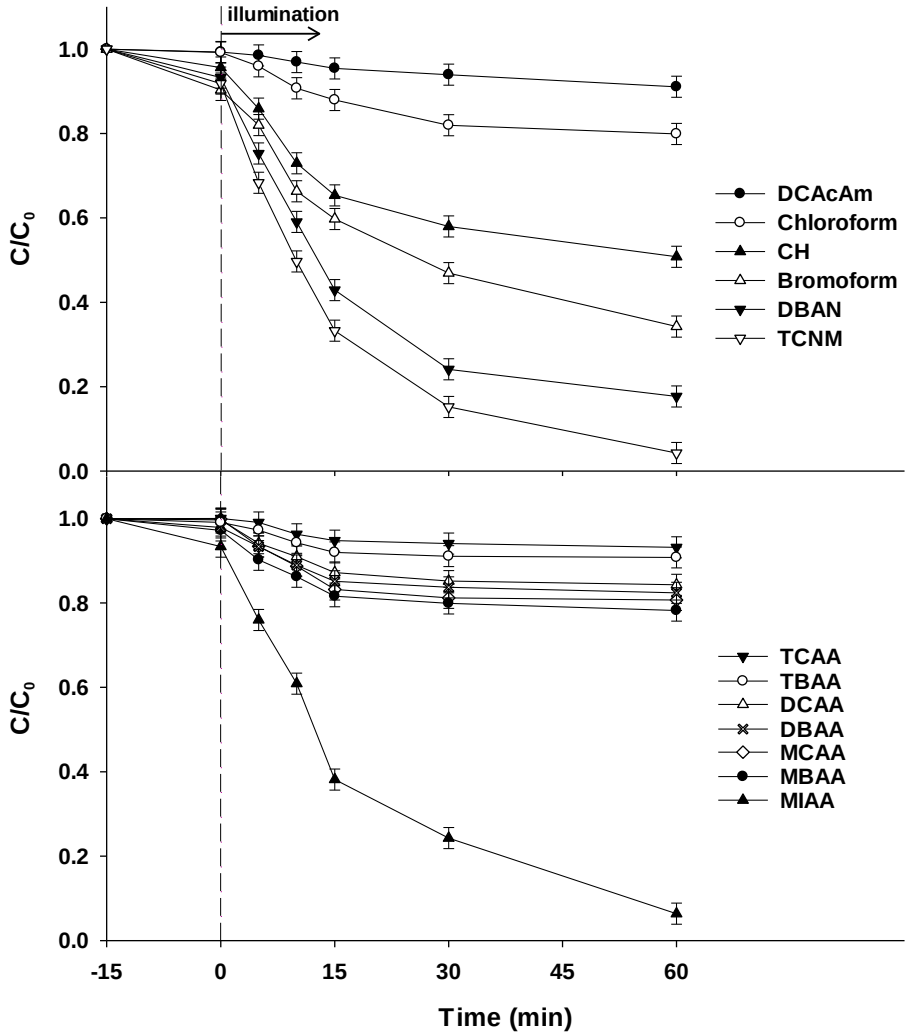

Figure 6.2: Degradation profile for individual DBPs treated with photo-fenton process under natural sunlight irradiation with 5 mg/L iron, 50 mg/L H_2O_2 and 0.2 mM EDDS at neutral pH

(Photolysis experimental conditions: date=07/03/2017, average solar radiation=1126 W/m^2, average temperature =28 °C. Error bars indicate standard deviations obtained from duplicate experiments.)

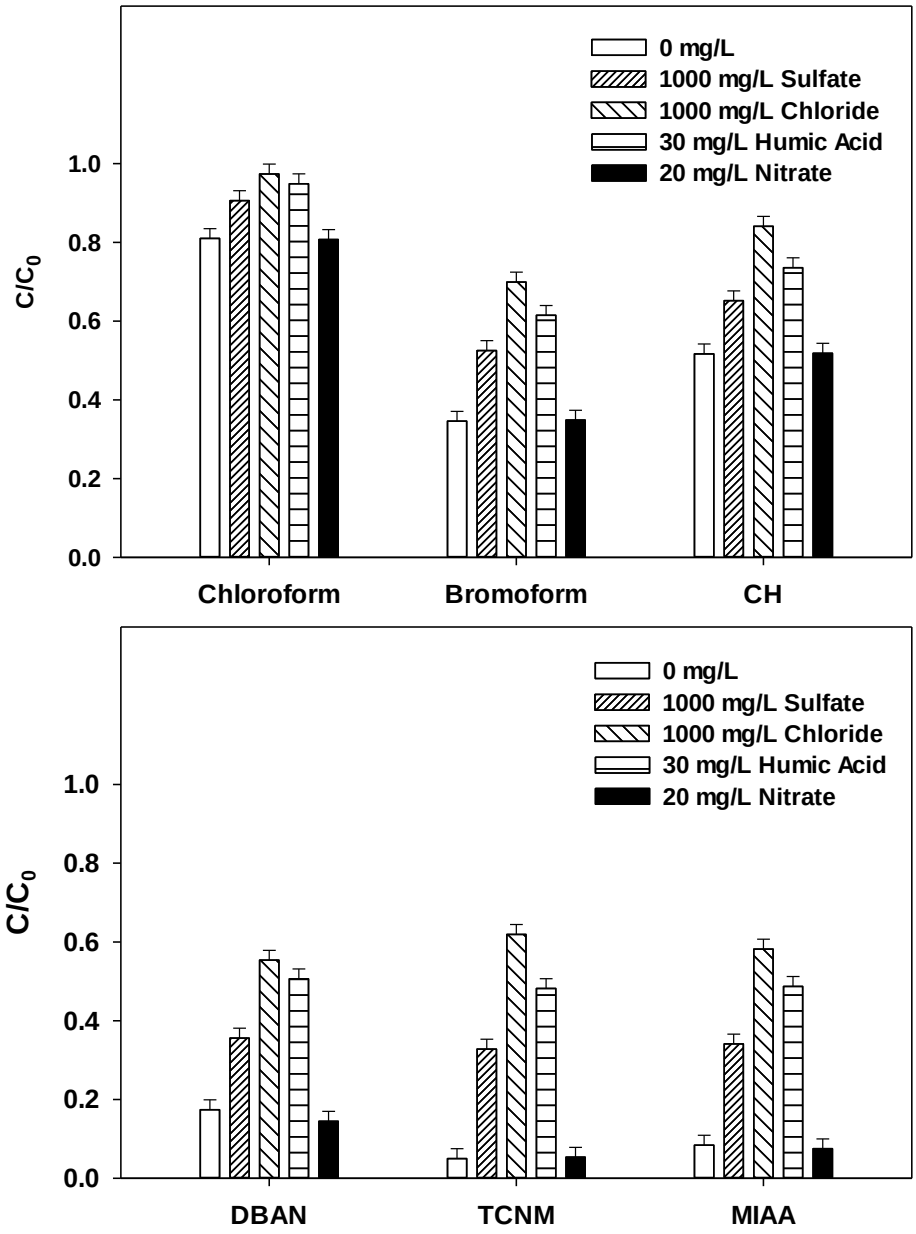

Figure 6.3: Effect of natural water contaminates on the degradation extents of individual DBPs by EDDS solar fenton process at neutral pH after 1-hr of natural sunlight irradiation

(5 mg/L iron, 50 mg/L H_2O_2 and 0.2 mM EDDS, photolysis experimental conditions: date=07/13/2017, average solar radiation=1086 W/m^2, average temperature =26 ℃. Error bars indicate standard deviations obtained from duplicate experiments.)

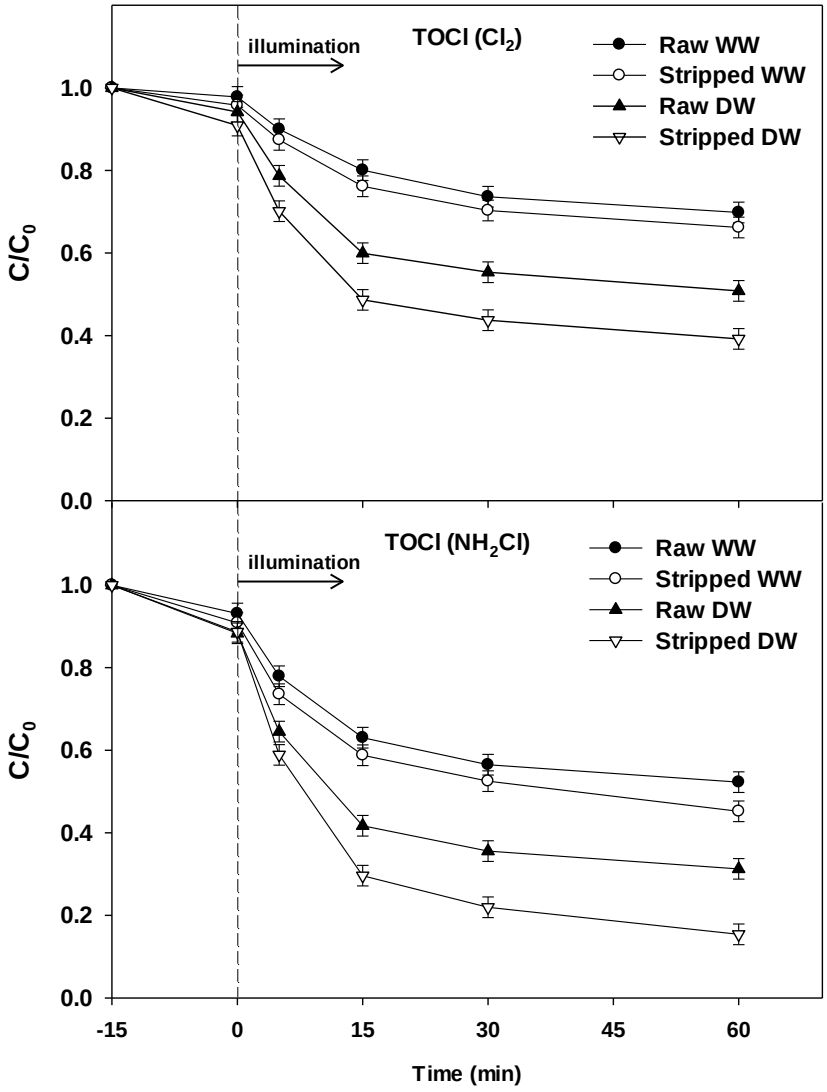

Figure 6.4: Effect of alkalinity on the degradation extents of TOCl (Cl_2) and TOCl (NH_2Cl) in real water and wastewater effluents by EDDS solar fenton process at neutral pH

(5 mg/L iron, 50 mg/L H_2O_2 and 0.2 mM EDDS, photolysis experimental conditions: date=07/28/2017, average solar radiation=1111 W/m^2, average temperature =27 °C. Error bars indicate standard deviations obtained from duplicate experiments.)

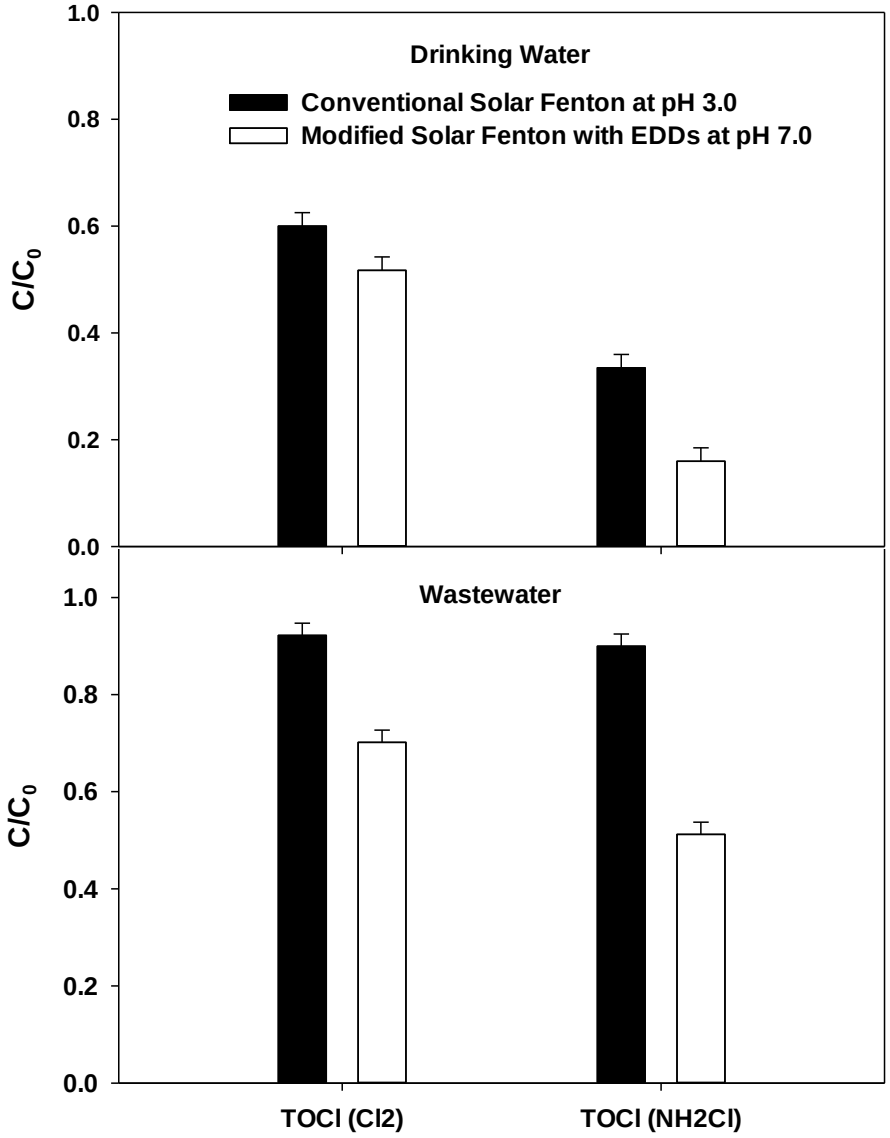

Figure 6.5: Comparison between the modified solar fenton by EDDS at neutral pH and conventional photo-fenton at pH 3.0 in the removal of TOCl (Cl_2) and TOCl (NH_2Cl) in real water and wastewater effluents after 1-hr of natural sunlight irradiation

(5 mg/L iron, 50 mg/L H_2O_2 and 0.2 mM EDDS, photolysis experimental conditions: date=08/08/2017, average solar radiation=1201 W/m^2, average temperature =28 ℃. Error bars indicate standard deviations obtained from duplicate experiments.)

CHAPTER SEVEN
SUMMARY

7.1 Conclusions

7.1.1 TOX Stability during Sample Preservation

To maintain TOX concentrations during storage at 4 °C, several factors need to be considered including 1) pH of TOX samples need to be acidic ≤ 2 using nitric acid for any of TOX species. Sulfuric and phosphoric acid can be used for TOCl and TOBr but must be avoided for TOI. 2) To remove halogen residuals, proper quenching agent must be used for each TOX species. Sodium sulfite, sodium thiosulfate and ascorbic acid were the ideal quenching agents for TOCl, TOBr and TOI, respectively. Uncontrolled overdosing (≥ 1000 μM) of quenching agents must be avoided regardless of quenching agent used. 3) TOX analysis should be conducted within 14 day of storage, however, for ideal results, analysis should be within 72 h. 4) During TOX analysis, TOX samples temperature must be at 4 °C through the AC adsorption step. Afterwards, AC columns must be rinsed with 15 mL of 1000 mg/L nitrate solution, to remove inorganic halides. This improved procedure for TOX analysis resulted in more than 90% recovery for all TOX species during 14 days of storage at 4 °C. Therefore, the TOX protocol by the Standard Methods (5340b) can be enhanced following the outcome of this study.

7.1.2 Fate of DBPs in Drinking Water Supplies by Natural Solar Photolysis

Natural solar photolysis can substantially reduce the concentration of TOX and individual DBPs under environmentally relevant conditions (pH, time, temperature). Brominated and iodinated DBPs were more photosensitive and degraded faster than chlorinated DBPs, suggesting that these highly toxic DBPs may have shorter lives than chlorinated analogues in natural environments. Direct solar photolysis was identified as

the major pathway for TOX and specific DBPs degradation and the contribution of nitrate, nitrite and sulfite induced indirect photolysis was insignificant under typical conditions. NOM in natural waters reduced DBPs and TOX solar degradation by light screening effect. The outcome of these studies provides a better understanding of the transformation of TOX and DBPs in surface waters by natural sunlight irradiation, which can help develop strategies to reduce the health risks associated with wastewater-derived DBPs during water reuse.

7.1.3 Removal of DBPs by Solar-based AOPs

The use of AOPs operated by natural sunlight showed promising results for removal of DBPs in municipal wastewater. Solar photocatalytic process by TiO_2 was very effective in removal of iodinated > brominated > chlorinated DBPs. At proper TiO_2 dose, phase identity, pH and photolysis time, half-lives for TOX species were in minutes. Oxidation by OH• radicals was considered as the major pathway for TOX degradation. Furthermore, limited contribution by hydrated electron that generates at the TiO_2 surface, may also induce TOX photocatalytic degradation in water. However, the presence of alkalinity in municipal wastewater reduce TOX solar photocatalytic degradation by TiO_2, due to scavenging properties of bicarbonate to OH• radicals.

Solar photo-fenton process also demonstrated significant degradation of TOX in water. However, most of specific DBPs were resistant to the process. OH• radicals were the only pathway responsible for the observed degradation of TOX. Common contaminants exist in municipal wastewater severely decrease the efficiency of the process including sulfate and chloride, since they react with dissolved iron forming inactive iron precipitants. The outcome of these studies indicated that solar AOPs can be

utilized for significant DBPs removal at municipal wastewater to protect drinking water supplies.

7.2 Application of Solar-based AOPs at WWTPs

The use of AOPs for water and wastewater treatment provide an effective attenuation and viable options for removal of toxic organic compounds in water. Several AOPs are already well established and operated at full-scale DWTPs and WWTPs especially the ones utilized UV light and/or ozone. However, these processes have many concerns regarding their operational costs including energy consumption and constant chemical input. Therefore, the use of natural sunlight to operate AOPs can provide promising, efficient, effective and environmentally-friendly alternative to reduce the costs of current AOPs while achieving the removal of the targeted toxic compound in water.

In this paper, the two solar AOPs processes were examined for DBPs degradation showed promising results. However, there operational costs and maintenance were very different. Solar photocatalytic process by TiO_2 required a certain load of TiO_2 nanoparticles. These particles can be either prepared in site or purchased, regardless, TiO_2 is affordable and can be easily acquired. However, the lower the sizes of TiO_2 particles the better for suspension, reactivity toward sunlight and possible adsorption of toxic organic compounds. On the contrary, this will increase the costs significantly, therefore lower than 21 nm that has been used in this process and is affordable, should not be necessary for DBPs removal in water. Solar TiO_2 photocatalytic process can also operate at neutral pH, thus no need for any chemical agents to adjust pH since wastewater effluent pH is discharged at neutral pH. On the other hand, to generate OH• radicals,

TiO_2 particles must be in suspension during the treatment to absorb sunlight. To meet this criteria, TiO_2 particles size must be < 300 nm and the treated water (contain targeted compounds) must be in motion during the photolysis time and that could be achieved by water recirculation pump. The major disadvantage of solar photocatalytic process by TiO_2 is the TiO_2 particles. Since solar TiO_2 photocatalytic process is heterogenous process, TiO_2 is cannot dissolve in water and must be removed prior to the discharge of wastewater effluent in surface water using a filter. Furthermore, several studies reported decrease in TiO_2 photo reactivity toward sunlight and thus decrease in OH• radicals formation over time. Consequently, after certain usage, TiO_2 load must be replaced to maintain stable DBPs degradation in wastewater effluent.

Solar Photo-Fenton process require the use of several chemicals to operate in the presence of sunlight including iron $Fe^{3+}/Fe^{2+}$and H_2O_2. Additionally, to operate the process at neutral pH, chelating agent must be used to maintain stable dissolved iron at higher pH values. The constant recycling of iron species in the presence of sunlight lead to constant release of OH• radicals, however, this also consume substantial amount of H_2O_2 that need to be continuously added throughout operation to achieve the required removal of DBPs. In addition to high consumption of chemicals, iron species can also precipitate leading to sludge formation that need to be removed. Additionally, chelating agents such as EDDS (organic compound) increase DOC concentration substantially in wastewater effluent. Therefore, this will require another treatment system to remove DOC prior to effluent discharge at surface water.

In comparison, solar photocatalytic process by TiO_2 process is much more energy efficient and does not has any major drawbacks that might increase contaminants in

wastewater effluent. Moreover, it does not produce any byproducts that need to be removed prior to effluent discharge. The only concern of this process is the constant replace of TiO_2 during treatment that could increase the operational costs. Therefore, more research is needed to investigate the possibility of re-photoactivate of exhausted TiO_2 particles or enhance TiO_2 surface by chemical doping to last for longer periods under operation. Therefore, solar photocatalytic process by TiO_2 process present combination of efficient, effective and environmentally-friendly process that can be applied for future water and wastewater treatment including removal of DBPs.

7.3 Recommendations for Future Work

1. The impact of other common quenching agents (arsenite, ammonium chloride and borohydride) on TOX concentration during storage at 4 and 20 °C.
2. The impact of the other natural biogeochemical degradation mechanism on stability of TOX in surface water, especially regarding biodegradation.
3. Research is needed to identify the contribution of generated hydrated electron reduction on the observed TOX degradation by solar TiO_2 photocatalytic process.
4. Investigation is necessary on the degradation of UTOX fraction through OH• radial attacks.
5. Pilot-scale and full-scale studies must be conducted on the applicability of solar photocatalytic process by TiO_2 at WWTPs for removal of DBPs from wastewater effluents.

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